

Organic Materials Challenges for 193 nm Imaging

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Received July 9, 1998

Introduction and Historical Perspective

The invention of the point contact transistor in 1947 heralded the dawn of the microelectronics era¹ which has had impact on every aspect of our lives. Materials chemistry in general and organic and polymer chemistry in particular have enabled the unprecedented advancements in microelectronics technology. The business is driven by the need to build devices that contain an increasing

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Omkaram Nalamasu joined Bell Laboratories, Lucent Technologies, in 1986 after completing his Ph.D. in chemistry at the University of British Columbia, Canada. He has made critical contributions to the deep-UV resist materials chemistry and process development areas. He has published over 90 papers, review articles, and book chapters on various aspects of photoresist materials design, synthesis, formulation, and process development and their implementation in IC fabrication. He has chaired and organized several national and international conferences on lithography and photoresist materials and delivered several invited and plenary talks at various national and international conferences, universities, and industrial institutions. He has also taught courses on materials for electronics in the U.S. and Japan through the American Chemical Society and the State University of New York continuing education organizations. He was a recipient of an R&D 100 award and serves on the editorial board of ACS books. He currently manages the optical lithography and imaging materials research programs at Bell Laboratories.

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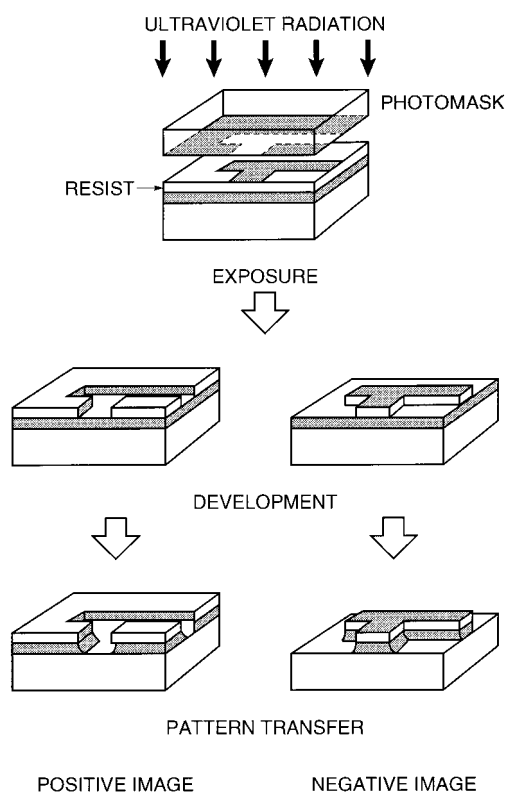


FIGURE 1. Schematic representation of the lithographic process.

number of individual circuit elements on a semiconductor material. Over time, device complexity and functionality have increased while minimum feature size has dramatically decreased.² The ability to shrink the feature size is critically dependent upon the technologies involved in the delineation of the circuit pattern. Thus, high-resolution imaging materials could be considered to be the cornerstone of today's device industry.

A modern integrated circuit is a complex three-dimensional structure of alternating, patterned layers of conductors, dielectrics, and semiconductor films. This structure is fabricated on an ultrahigh-purity wafer substrate of a semiconducting material such as silicon. The performance of the device is, to a large degree, governed by the size of the individual elements. As a general rule, the smaller the elements, the higher the device performance will be. The structure is produced by a series of steps used to precisely pattern each layer. The patterns are formed by lithographic processes that consist of two steps: (i) delineation of the patterns in a radiation-sensitive thin polymer film called the resist and (ii) transfer of that pattern using an appropriate etching technique. A schematic representation of the lithographic process is shown in Figure 1.²

An overwhelming preponderance of devices continue to be fabricated via "conventional photolithography" employing 350–450 nm light. Incremental improvements in tool design and performance with concomitant refinements in the novolac/diazonaphthoquinone resist materials chemistry and processing have allowed the continued use of this technology to produce ever smaller features.

- I. PHOTOGENERATION OF ACID
 II. DEPROTECTION OF MATRIX POLYMER

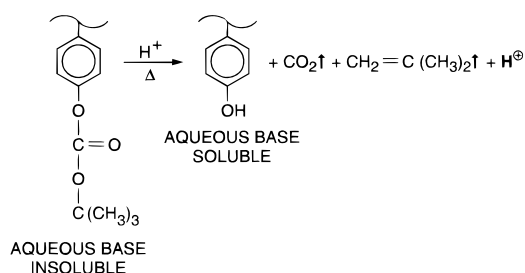


FIGURE 2. Chemistry associated with a chemically amplified resist system based upon poly(*tert*-butoxycarbonyloxystyrene).

The cost of introducing 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. As device feature sizes approached 0.25 μm and the industry moved toward using 248 nm excimer laser UV light as the exposing wavelength for advanced lithographic applications, the materials community saw the first revolutionary change in resist materials chemistry to be adopted. Conventional photoresists are not appropriate for use with the UV light sources principally because their absorbance is too high to allow uniform imaging through a practical resist film thickness (0.5–1 μm).³ Additionally, the available light at the exposure plane of commercial exposure tools is insufficient to provide for manufacturable processes when the quantum efficiency of a resist is less than 1.

The breakthrough that ultimately led to the adoption of 248 nm lithography as the technology of choice for advanced device fabrication was the announcement of what has been termed the "chemically amplified" resist mechanism. The pioneering work relating to the development of chemically amplified resists based on deprotection mechanisms was carried out by Ito, Willson, and Frechet.⁴ These initial studies dealt with the catalytic deprotection of poly(*tert*-butoxycarbonyloxy)styrene (TBS) in which the thermally stable, acid-labile *tert*-butoxycarbonyl group is used to mask the hydroxyl functionality of poly(vinylphenol). As shown in Figure 2, irradiation of TBS films containing small amounts of an onium salt, such as diphenyliodonium hexafluoroantimonate, with UV light liberates an acid species that upon subsequent baking catalyzes cleavage of the protecting group to generate poly(vinylphenol). While this reaction will take place very slowly at room temperature, it is much faster at 100 °C, requiring only a few seconds to reach completion. In the absence of an acidic species, the protected polymer undergoes no degradation during prolonged heating at that temperature. 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 tone images, depending upon the developer.

Since the initial reports regarding chemically amplified resist mechanisms in 1980, numerous research groups have expanded on this revolutionary concept. Both alternate protective groups and parent polymers have been utilized. Generally, thermally stable, acid-labile substituents are desirable as protective groups for aqueous-base-soluble parent polymers. Some typical examples of protective groups that have been employed include *tert*-butyl ethers and esters, tetrahydropyranyl ethers, α,α -dimethylbenzyl esters, and ketals and acetals. Alternate polymer backbones include poly(hydroxystyrene), poly(vinylbenzoic acid), and poly(methacrylic acid). Additionally, high glass transition temperature (T_g) polymers based on N-blocked maleimide/styrene resins and substituted styrene-sulfone copolymers have been explored.³ Notably, the first commercially available positive 248 nm resist was introduced in 1990 after almost 10 years of research, and was based on the copolymer derived from *tert*-butoxycarbonyloxystyrene and sulfur dioxide used in conjunction with a nitrobenzyl tosylate photoacid generator material.⁵

Since the conception of chemical amplification mechanisms for microlithographic applications almost two decades 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 chemistries for use with future lithographic technologies.

193 nm Materials Design Issues

The first experiments demonstrating the feasibility of UV light as an imaging source for lithography occurred at Bell Laboratories in 1975.⁶ Bowden and Chandross demonstrated the concept using poly(butene-1-sulfone) which, upon exposure to 185 nm light, exhibited a sensitivity of 5 mJ/cm². The drive toward still smaller features, fueled by a desire to maintain the availability of optical lithography in the device production environment, led to research and development efforts aimed at developing a production-worthy 193 nm lithographic technology.⁷ However, the opacity of traditional UV and deep-UV (DUV) organic matrix resins and photoresist components at 193 nm necessitates a paradigm shift in the design of 193 nm resist materials. The challenge to a resist chemist has been to design a system having an aliphatic framework that is functionally identical to the current commercial DUV and I- or G-line resist materials based upon poly(hydroxystyrene) and novolac resin chemistry.

Table 1. Key Resist Lithographic Properties and How They Relate to Molecular Properties of Resist Components

lithographic parameter	molecular characteristic
absorption	no olefinic or aromatic moiety
etching stability	high levels of structural carbon, low oxygen content
aqueous base solubility	base-solubilizing groups such as OH, COOH, NH, etc.
substrate adhesion	presence of polar moieties
sensitivity or photospeed	catalytic chain length for acidolysis, quantum yield for acid generation, acid strength, protective group chemistry
postexposure delay and substrate sensitivity	catalytic chain length for acidolysis, protective group chemistry, acid strength
outgassing	protective group and photoacid generator chemistry
aspect ratio of images	surface tension effects and mechanical strength of materials
low metal ion content manufacturability and cost	synthesis and scale-up methodology synthesis and materials scale-up methodology and lithographic process requirements

Photolithography using a 193 nm (Ar–F excimer laser) light source is the leading candidate for future microelectronics device fabrication using 0.13–0.18 μm design rules.⁷ Many of the materials requirements for a 193 nm resist are identical to those set forth for previous generations of optical lithography. The requirements of sensitivity, contrast, etching resistance, and purity are ubiquitous. The issue of sensitivity is readily addressed through application of “chemically amplified resist” design principles developed for 248 nm materials. Contrast, or the rate at which a given material responds to incident irradiation, must be high to ensure high-resolution patterning. While affected by many materials parameters including absorbance, dissolution behavior, T_g , etc., perhaps one of the most significant factors for 193 nm imaging is absorption, or rather the opacity of a given material. Traditional UV and 248 nm chemically amplified organic resists are simply too opaque at 193 nm precluding their use in single-layer schemes at this wavelength. Equally, if not more challenging, is the issue of etching resistance. For a material to be implemented into device fabrication, it has to effectively withstand the plasma and reactive-ion-etching environments that are used to transfer printed features into a given device substrate. Such etching resistance has traditionally been achieved through the use of aromatic moieties in the resist polymer.⁸ Primarily through the efforts of Ohnishi and Kunz, it has been proposed that the key factors affecting etching resistance are the “effective carbon content” of a material. Thus, it was predicted that high alicyclic content polymers should approach the performance of aromatic resins in plasma environments.⁹ Table 1 lists key lithographic performance parameters and how they relate to critical materials molecular characteristics. Understanding the performance criteria and how each is affected by choice of materials chemistry allows definition of structures that can be successfully used in 193 nm imaging materials. For instance, base solubility in the vast majority of matrix polymers used for lithography arises from the presence of either phenolic hydroxides or carboxylic acid moieties.

Introduction of these oxygen-rich OH and COOH groups into aliphatic polymers generally effects base solubility, but also decreases the resistance of the resultant polymers to the etching processes used to transfer the images into device substrates, particularly during patterning of metal and polysilicon films where especially corrosive gases are employed.

The initial focus for designing 193 nm resists centered on derivatized acrylate and methacrylate copolymers. By and large, these polymers are effectively transparent at 193 nm and exhibit excellent resolution, but lack plasma-etching resistance and other requisite materials properties for lithographic performance. The first example of a high-speed 193 nm acrylate resist was demonstrated in a collaboration between MIT Lincoln Laboratory and IBM. This material consisted of a methacrylate terpolymer containing acidolytically labile *tert*-butylmethacrylate repeat units formulated with a diphenyliodonium triflate onium salt photoacid generator (PAG).^{7b,10} While successful in attaining excellent resolution and photospeed, the materials were excessively soluble (both protected and unprotected regions) in the industry standard 0.262 N tetramethylammonium hydroxide (TMAH) developer and showed poor etching properties because of the relatively high oxygen content of the polymer. The etching performance is aggravated by the inherent susceptibility of methacrylate-based polymers to undergo both radiation and thermally induced degradation. Use of large alicyclic groups in the side chain, in combination with dissolution inhibitors (DI) that are high in structural carbon, has improved the compatibility of these systems with 0.262 N TMAH, but etching stability remains to be addressed to alleviate the pattern transfer problems. The etching stability issue is further compounded by aspect ratio considerations such as surface tension effects during development, and the inherent mechanical stability of the polymer predicates the usable film thickness to be at or below an image aspect ratio of 4. This translates into a thickness limit of 0.6–0.42 μm for 0.15 and 0.13 μm design rules, respectively, which is significantly below that used in manufacturing today.

Thus, the fundamental design challenge that has emerged appears to be the necessary tradeoff between plasma-etching resistance and requisite materials properties for lithographic performance. On the whole, high carbon content copolymers functionalized with pendant alicyclic moieties possess adequate etching resistance but tend to be brittle, display poor adhesion, and have suboptimal imaging characteristics due to their aqueous base solubility. Decreased alicyclic carbon content results in improved lithographic performance at the cost of etching resistance. Examples of substituents that have been employed include menthyl,¹¹ adamantyl,¹² isobornyl,¹³ and tricyclodecyl.^{7a}

Recent approaches to addressing this fundamental design challenge include (i) careful tailoring of polymer properties to maximize lithographic performance with minimal sacrifice in etching performance and (ii) development of three-component systems in which high carbon

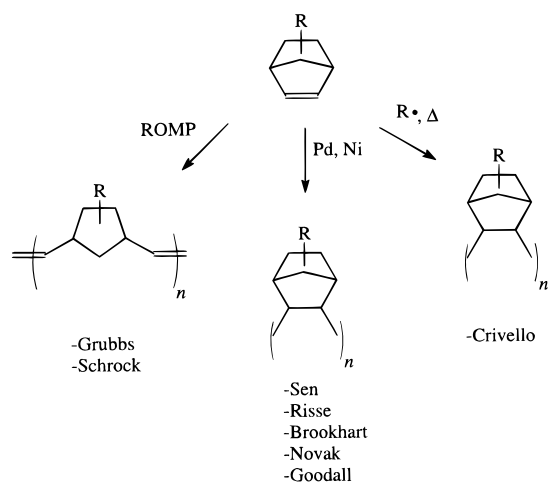


FIGURE 3. Schematic representation of available routes to alicyclic backbone polymers.

content alicyclic additives not only serve as dissolution inhibitors but also enhance the resistance of the matrix as a whole to plasma environments.

Alicyclic Polymers for 193 nm Imaging

As noted above, the first materials platforms that were examined for the purpose of providing transparent, 193 nm imagable matrixes were based on methacrylate resin chemistry.^{7,10–13} While methacrylate-based resist platforms are attractive from an economic perspective, they suffer from the fundamental drawback of possessing a linear, oxygen-rich scaffold whose poor plasma-etching stability can be offset only partially by functionalization with more stable pendant groups. In a more ideal resist platform, greater intrinsic plasma stability might be imparted through incorporation of alicyclic, etching-resistant moieties directly into the polymer backbone. In addition, minimizing oxygen content by designing oxygenated functionalities to play only necessary imaging, adhesion, and solubilizing roles would be beneficial. Alternative routes to achieve the goal of an “all alicyclic backbone” are shown in Figure 3 for the alicyclic alkene norbornene. These routes are the ring-opening metathesis polymerization (ROMP),¹⁴ the metal-catalyzed vinyl polymerization,¹⁵ and radical-promoted vinyl polymerization.¹⁶ Because of the potential for metal ion contamination, neither ROMP nor metal-catalyzed vinyl polymerization is a currently “realistic route” for achieving an all alicyclic backbone polymer because of the high cost associated with effecting <5 ppb metal contamination of the final polymer.¹⁷

Cycloolefin-maleic anhydride alternating copolymers may provide an attractive alternative to methacrylate-based matrix resins.¹⁷ Compelling features of these copolymers include (a) facile synthesis via standard radical polymerization, (b) a potentially large pool of cycloolefin feedstocks, and (c) a generic structural motif that incorporates alicyclic structures directly into the polymer backbone and provides a latent water-solubilizing group that may also be useful for further structural elaboration. A large number of cycloolefins are known to copolymerize

with maleic anhydride. As a rule, they yield high- T_g copolymers with a 1:1 alternating structure. Cyclic diolefins undergo transannular cyclopolymerizations that may be accompanied by substrate-specific complications. While we have screened a number of cycloolefins as substrates, efforts to date have concentrated largely on norbornene and various substituted analogues.

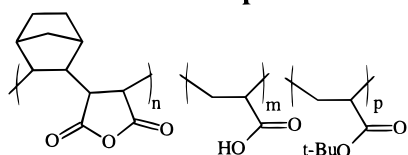
Norbornene-maleic anhydride copolymerizations¹⁸ were first described in a patent that provided two key insights: (i) copolymerization provides a material with a 1:1 composition regardless of monomer feed ratio and (ii) incorporation of small percentages of other vinyl monomers without disruption of the essentially alternating nature is tolerated. The alicyclic monomer readily undergoes free radical induced copolymerization with maleic anhydride to afford an alternating, high- T_g polymer. While soluble in polar organic solvents such as cyclohexanone and methyl isobutyl ketone, the copolymer is insoluble in aqueous media and appears hydrolytically robust.¹⁷

Aqueous base solubility can be induced in this alternating copolymer via incorporation of acrylic acid. Free radical polymerization of the cycloolefin and maleic anhydride in the presence of acrylic acid and/or its derivatives provides a controllable method for synthesizing aqueous base soluble resins.¹⁷ Such materials were readily soluble in standard organic solvents used to spin coat resist films, and additionally were soluble in aqueous base media such as 0.262 N tetramethylammonium hydroxide, the developer of choice for the electronics industry. Notably, thin films of these polymers cast onto quartz substrates display excellent transparency at both 248 and 193 nm, with the absorbance per micrometer of typical poly(norbornene-*co*-maleic anhydride-*co*-acrylic acid) materials being approximately 0.2.

These norbornene-based matrix resins can be used in a variety of resist approaches (Figure 4). The strategies that have been examined include the use of a protected polymer in conjunction with a PAG in a “two-component” chemically amplified resist process, a three-component system using the parent acidic terpolymer, a DI, and a PAG, and a hybrid approach that uses both a DI and a partially protected matrix.^{17,19} The latter two approaches afford added flexibility in the design of a resist for the application at hand, and thus DI chemical design issues will be examined more closely.

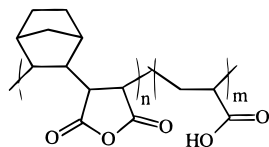
Dissolution Inhibitor Design. Dissolution inhibitor use in resist applications predates their application to microelectronics and starts with the use of diazonaphthoquinones (DNQ) in novolak resins for the manufacture of printing plates.² For conventional photolithography using 365 and 435 nm light, multifunctional DNQs have been shown to dramatically improve contrast and side-wall profiles relative to monofunctional analogues in novolak-based resists. For instance, one of the more commonly used multifunctional DNQs is a trihydroxybenzophenone functionalized with multiple DNQ moieties. In this approach, the fully converted tris(indenecarboxylic acid) is formed in appreciable amounts only above a certain threshold energy, thereby greatly increasing the nonlinear

Two Component Resists

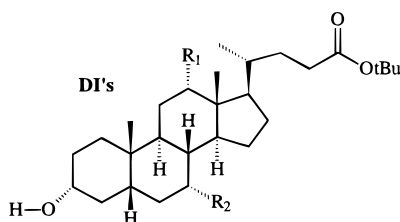


PAG's: Onium Salts

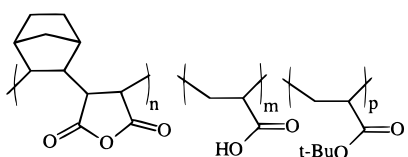
Three Component Resists



PAG's: Onium Salts



Hybrid Resists



DI's, PAG's

FIGURE 4. Structures associated with norbornene-maleic anhydride resist options.

relationship between exposure and the dissolution rate of the resist.²⁰ These principles lay the groundwork for the design of aliphatic DIs for 193 nm applications.

The first example of an aliphatic DI was based on cholate ester chemistry, namely, 2-nitrobenzylcholate, which was used in methyl methacrylate copolymers for 240–260 nm resist applications.²¹ The rationale used to select the steroid as the basis for the design of a DI

included its large molecular volume that could be very effectively converted from an aqueous-base-insoluble form, namely, an ester, to the exceptionally aqueous-soluble parent acid. The solubility of sodium cholate in water is 500 g/L. The presence of the hydroxyl substituents on the molecular framework of this ester provides for sites that allow interaction of the DI with the surrounding polar matrix, thus promoting compatibility between the components. High-contrast imaging is obtained with such systems because of the large molar volume of resist that can be made hydrophilic by a single bond scission. Thus, the aliphatic steroid possesses many of the desired characteristics that are present in conventional DNQ inhibitors.

Shortly after the report of the utility of 2-nitrobenzyl cholate, *tert*-butyl cholate was described for use in various phenolic matrixes for long UV and 248 nm deep-UV chemically amplified resist applications.²² In this instance, the bond scission is induced through acidolytic cleavage of the ester moiety upon photolysis of a PAG additive. The applicability of this class of steroids as inhibitors for 193 nm applications was demonstrated a decade later.^{7b}

Building further on the strategies that have proven effective in the design of DNQs for conventional novolac-based resists, a series of dimeric and oligomeric cholate-based DIs were synthesized via condensation polymerization of the cholate derivative with a short chain alkyl acid or diacid halide as shown in Figure 5.¹⁹ In all cases, the *tert*-butyl protecting group was employed as the acid-sensitive moiety on the polymer and DIs. The oligomeric dissolution inhibitors are very soluble in norbornene-maleic anhydride-acrylate polymers and exhibit no tendency toward phase separation at loadings even as high as 40 wt %. The T_g data indicate that there is a strong interaction between the DI and polymer, a necessary condition for both compatibility and dissolution inhibition. For example, the T_g values of the polymer, DI, and 35% oligomeric DI in the polymer film were 190, 100, and 185 °C, respectively. No interaction between the components would result in a T_g of about 158 °C, the geometric mean between the two components. Preliminary NMR studies also indicate a strong interaction. These interactions in turn lead to enhanced lithographic performance of the composite resist material. Generally, the oligomeric

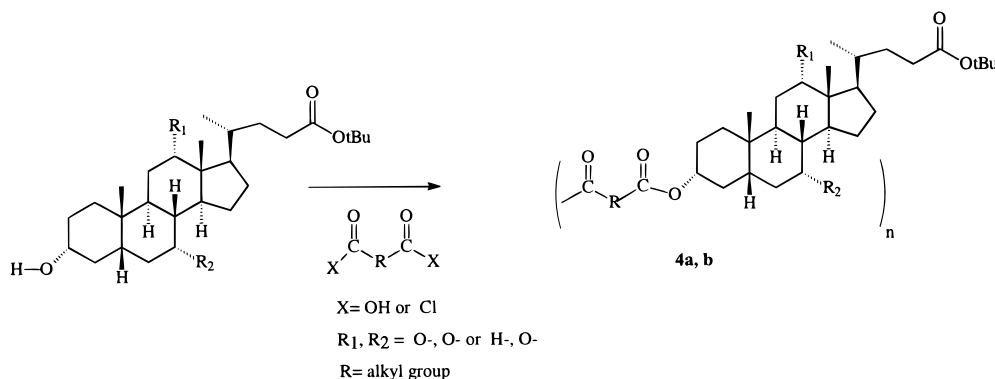


FIGURE 5. Synthesis and structure of *tert*-butyl cholate-based dissolution inhibitors.

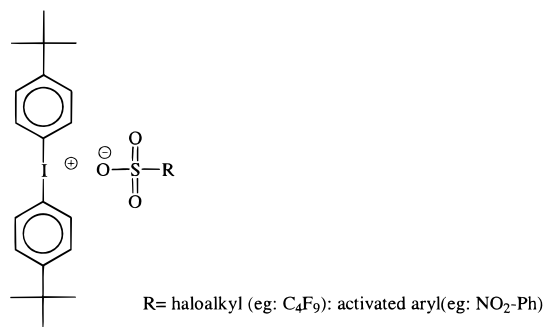


FIGURE 6. Representative photoacid generator structure.

inhibitors not only improved the contrast and solubility of the exposed areas in 0.262 N TMAH but also reduced the unexposed film loss. The optimum adhesion and contrast were obtained by using a mixture of oligomeric dissolution inhibitor with a polar “monomeric” material such as *tert*-butyl cholate.

Photoacid Generator Design Issues. While aromatic PAGs are highly absorptive at 193 nm, they are only needed in small quantities (typically <5%) in resist formulations. Consequently, 193 nm resists could be designed using the same PAGs as those that are in use with 248 nm resists. In addition to absorption, the considerations in designing a PAG are solubility, volatility of both the PAG and its photoproducts, acid strength, cost,

and toxicity.^{5c} For *tert*-butyl-substituted materials, high acid strength (often superacids are required) and high postexposure bake (PEB) temperatures are required for complete removal of the ester appendage. Examples of applicable chemistries include photogenerated acid of perfluoroalkyl sulfonic acids, or aryl sulfonic acids highly activated with electron-withdrawing groups.^{19,23} One example is given in Figure 6.

Base Additives. While the acid-catalyzed deprotection reaction affords many advantages to designing sensitive lithographic materials, it induces several potential phenomena that unaddressed would preclude application of such mechanisms in “real-world” manufacturing. Some typical problems associated with chemically amplified technologies include diffusion of the photogenerated acid and depletion of acid at the resist–air interface. Depletion of acid can arise from either volatilization of the acidic species or more significantly neutralization of the minute amounts of acid present at the resist–air interface by adventitious airborne amines present in most environments.²⁴ Acid diffusion is manifested as erosion or rather “slimming” of resolved lines with delays in postexposure baking to effect deprotection, while either volatilization or neutralization of the catalyst results in what is termed “T-topping” of lines, a phenomenon that also is aggravated upon delays in baking. Figure 7 depicts examples

TIME DELAY WITHOUT OVERCOAT

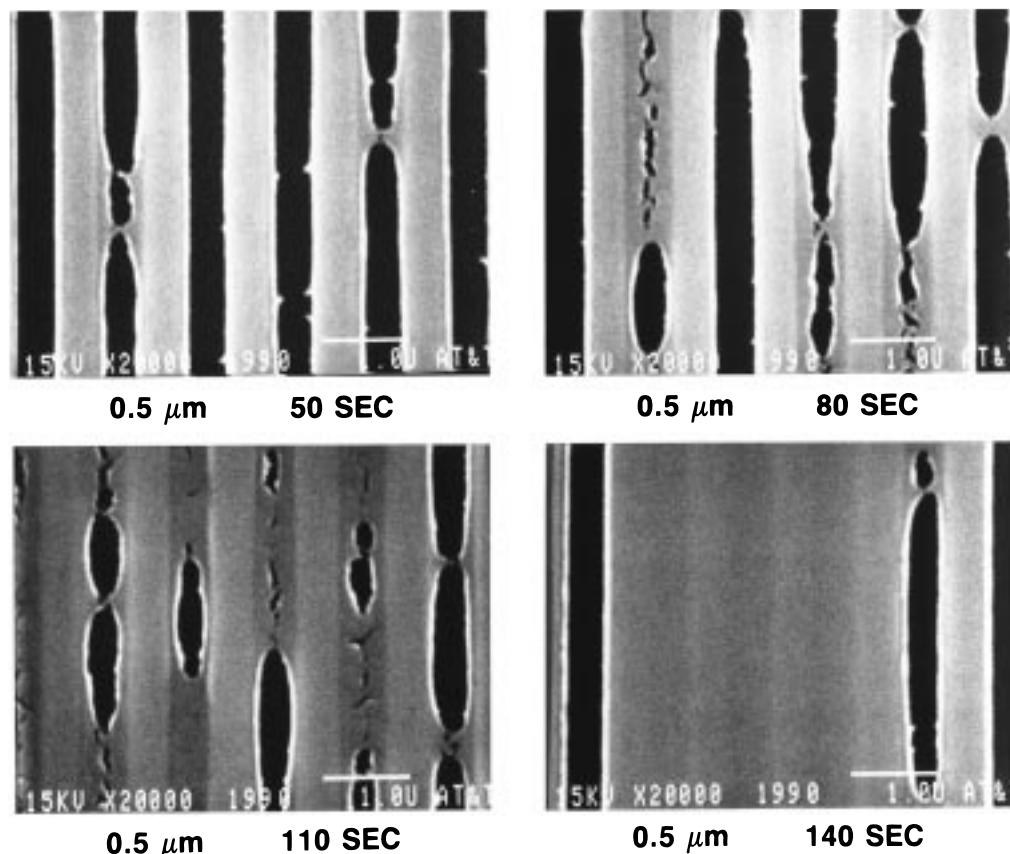


FIGURE 7. SEM micrograph depicting the effects of airborne amines on chemically amplified resist performance as a function of time.

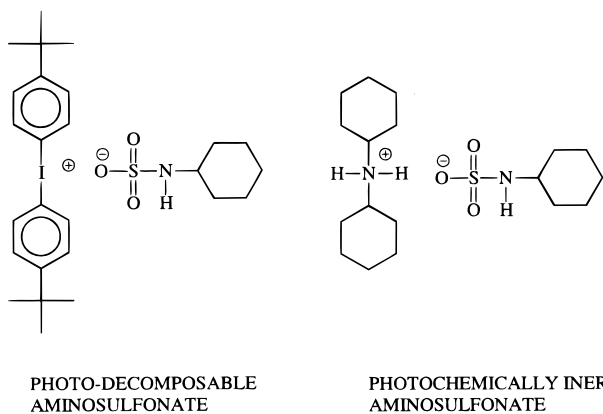


FIGURE 8. Structural representation of a photodecomposable aminosulfonate.

of this latter issue. Base additives are known to reduce line width slimming by reducing the diffusion of acid.²⁵ In the case of T-topping, base additives have been shown to alleviate this issue through either reduced volatilization of acid via decreased diffusion or, alternatively, creation of a low, uniform concentration of amine in the resist film which acts to overwhelm airborne basic contaminants depositing at the surface of the resist.²⁵

The possibility of utilizing photodecomposable aminosulfonate moieties capable of affording free aminosulfonic acids has been investigated.²⁶ Since in ester form these materials are inherently basic, yet upon exposure to light generate an acid, they have been called photodefinable bases (PDB). The PDB approach is very advantageous to the design of sensitive 193 nm resist materials to minimize glass damage without impacting exposure tool throughput. It has been shown that the use of such materials leads to enhanced resist sensitivity because the aminosulfonate moiety is partially removed in the exposed resist film but remains unchanged in the unexposed areas where its basic properties act to limit diffusion. For instance, Figure 8 shows the structure of two different cyclamate materials which were employed as base additives in a 193 nm single-layer resist based on a norbornene/maleic anhydride-onium salt resist platform: the photodecomposable moiety afforded a material with a resolution dose of 22 mJ/cm², while the formulation containing the inert compound was far less sensitive (50 mJ/cm²).²⁶ These materials effectively moderate the diffusion length of typical acids used in 193 nm chemically amplified resist formulations and impart much desired time delay stability.

Lithographic Performance

Molecular level understanding of materials issues and how those issues relate to key lithographic performance criteria allows for the design of effective, manufacturable 193 nm lithographic materials that may be implemented into next generation device fabrication facilities utilizing 193 nm exposure technologies. Materials based upon poly(norbornene-*co*-maleic anhydride-*co*-*tert*-butyl acrylate-*co*-acrylic acid) formulated with *tert*-butyl cholate dissolution inhibitors, diphenyliodonium nonaflate photoacid genera-

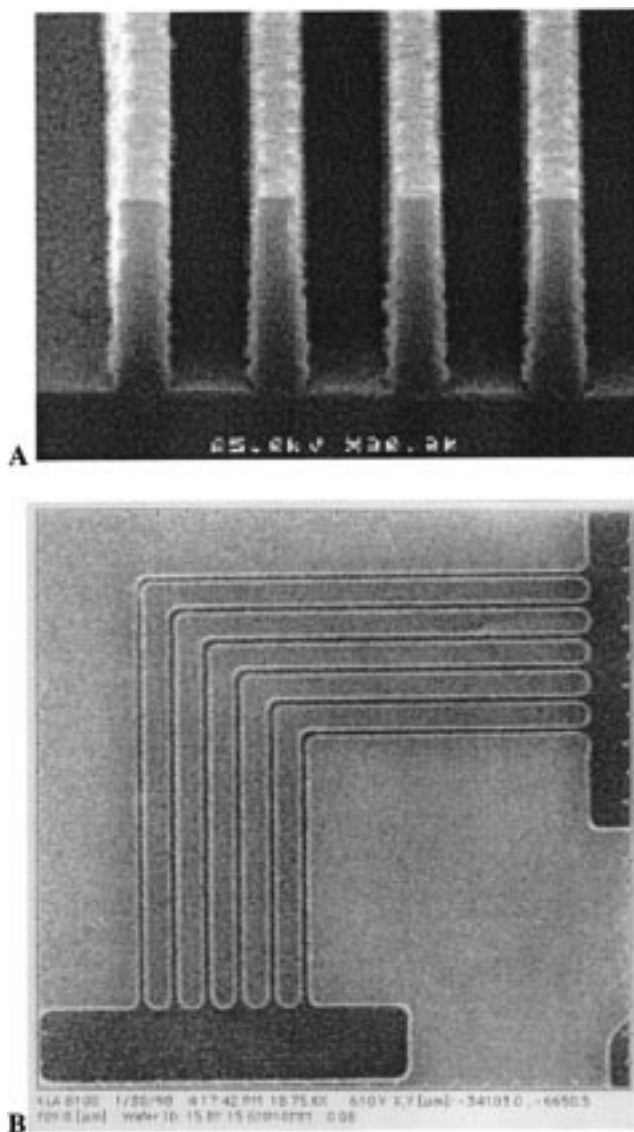


FIGURE 9. SEM micrographs depicting (a) 0.15 μm line/space images printed with a traditional mask and (b) 80 nm patterns printed with "phase-shift" mask technology in a norbornene-maleic anhydride-based 193 nm resist.

tors, and photodefinable bases such as those described above are effective high-resolution imaging materials. Figure 9 depicts SEM micrographs of typical patterns obtained with these materials.

Conclusion

A 193 nm resist design methodology was elucidated by examining the molecular structure–lithographic property relationships for key resist components such as the matrix polymer, dissolution inhibitor, photoacid generator, and base additive. The work demonstrates some of the challenges that recur frequently in designing not only photoresist materials, but any material for a given application. For 193 nm materials, the primary challenge of incorporating requisite imaging and lithographic properties was met by the design of cycloolefin-maleic anhydride polymers, cholate dissolution inhibitors, and photodecomposable bases. Fundamental studies into the materials

properties and the interactions between resist components enabled formulation of high-performance resists that display extremely reproducible lithographic properties. Specifically, this requires careful manipulation of a large number of physical properties that govern solubility, sensitivity, image fidelity, etc. Design principles governing different properties may not always work in concert; a functional resist design will, in the end, reflect multiple compromises and tradeoffs.

References

- (1) Bardeen, J.; Brattain, W. H. The Transistor, a Semiconductor Triode. *Phys. Rev.* **1948**, *74* (2), 230.
- (2) Thompson, L. F.; Willson, C. G.; Bowden, M. J. *Introduction to Microlithography*; ACS Professional Reference Book; American Chemical Society: Washington, DC, 1994.
- (3) (a) Willson, C. G.; Bowden, M. J. Organic Resist Materials. In *Electronic and Photonic Applications of Polymers*; Bowden, M. J., Turner, S. R., Eds.; ACS Advances in Chemistry Series 218; American Chemical Society: Washington, DC, 1988; pp 75–108. (b) Iwayanagi, T.; Ueno, T.; Nonogaki, S.; Ito, H.; Willson, C. G. Materials and Processes for Deep-UV Lithography. *Ibid.*; pp 109–224. (c) Reichmanis, E.; Houlihan, F. M.; Nalamasu, O.; Neenan, T. X. Chemical Amplification Mechanisms for Microlithography. *Chem. Mater.* **1991**, *3*, 394.
- (4) (a) Willson, C. G.; Ito, H.; Frechet J. M. J. New UV Resists with Negative or Positive Tone. *Digest of Technical Papers—1982 Symposium on VLSI Technology*, Kanagawa, Japan, September 1982; p 86. (b) Willson, C. G.; Ito, H.; Frechet, J. M. J.; Tessier, T. G.; Houlihan, F. M. Approaches to the Design of Radiation-Sensitive Polymeric Imaging Systems with Improved Sensitivity and Resolution. *J. Electrochem. Soc.* **1986**, *133*, 181.
- (5) (a) Houlihan, F. M.; Neenan, T. X.; Reichmanis, E.; Kometani, J. M.; Chin, T. Design, Synthesis, Characterization and Use of All-Organic Nonionic Photogenerators of Acid. *Chem. Mater.* **1991**, *3*, 462. (b) Kanga, R. S.; Kometani, J. M.; Reichmanis, E.; Hanson, J. E.; Nalamasu, O.; Thompson, L. F.; Heffner, S. A.; Tai, W. W.; Trevor, P. Synthesis and Characterization of Poly[4-((*tert*-butoxycarbonyloxy)styrene-sulfone)]. *Chem. Mater.* **1991**, *3*, 660. (c) Houlihan, F. M.; Reichmanis, E.; Thompson, L. F.; Tarascon, R. G. Chemically Amplified Resists: Effect of Polymer and Acid Generator Structure. In *Polymers in Microlithography*; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; ACS Symposium Series 412; American Chemical Society: Washington, DC, 1989; pp 39–56. (d) Houlihan, F. M.; Nalamasu, O.; Kometani, J. M.; Reichmanis, E. A Retrospective on 2-Nitrobenzyl Sulfonate Photoacid Generators. *J. Imaging Sci. Technol.* **1997**, *41* (1), 35.
- (6) (a) Bowden, M. J.; Chandross, E. A. Poly(Vinyl Arene Sulfones) As Novel Positive Photoresists. *J. Electrochem. Soc.* **1975**, *122*, 1370. (b) Feldman, M.; White, D. L.; Chandross, E. A.; Bowden, M. J.; Appelbaum, J. Reduced Diffraction with Deep-UV Photoresist Exposure. *Proceedings, Kodak Microelectronics Seminar*, Eastman Kodak: Rochester, NY, 1975; p 40.
- (7) (a) Nakano, K.; Maeda, K.; Iwasa, S.; Ohfuji, T. Positive Chemically Amplified Resist for ArF Excimer Laser Lithography Composed of a Novel Transparent Photoacid Generator and an Alicyclic Terpolymer. *Proc. SPIE* **1995**, *2438*, 433. (b) Allen, R. D.; Wan, I. Y.; Wallraff, G. M.; DiPietro, R. A.; Hofer, D. C.; Kunz, R. R. Resolution and Etch Resistance of a Family of 193 nm Positive Photoresists. *J. Photopolym. Sci. Technol.* **1995**, *8*, 623. (c) Nalamasu, O.; Wallow, T. I.; Houlihan, F. M.; Reichmanis, E.; Timko, A. G.; Dabbagh, G.; Cirelli, R. A.; Hutton, R. S.; Novembre, A. E. Revolutionary and Evolutionary Resist Design Concepts for 193 nm Lithography. *Future Fab Int.* **1997**, *1* (2), 159.
- (8) Willson, C. G. In *Introduction to Microlithography*; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.; ACS Professional Reference Book, American Chemical Society: Washington, DC, 1994; pp 139–267.
- (9) (a) Ohnishi, Y.; Mizuko, M.; Gokan, H.; Fujiwara, S. Post Irradiation Polymerization of E-Beam Negative Resists: Theoretical Analysis and Method of Inhibition. *J. Vac. Sci. Technol.* **1981**, *19* (4), 1141. (b) Gokan, H.; Esho, S.; Ohnishi, Y. Dry Etch Resistance of Organic Materials. *J. Electrochem. Soc.* **1983**, *130* (1), 143. (c) Kunz, R.; Palmateer, S. C.; Forte, A. R.; Allen, R. D.; Wallraff, G. M.; DiPietro, R. A.; Hofer, D. C. Limits to Etch Resistance for 193 nm Single-Layer Resists. *Proc. SPIE* **1996**, *2724*, 365.
- (10) Kunz, R. R.; Allen, R. D.; Hinsberg, W. D.; Wallraff, G. M. Acid-Catalyzed Single-Layer Resists for ArF Lithography. *Proc. SPIE* **1993**, *1925*, 167.
- (11) Shida, N.; Ushirogouchi, T.; Asakawa, K.; Nakase, M. Novel ArF Excimer Laser Resists Based on Menthyl Methacrylate. *J. Photopolym. Sci. Technol.* **1996**, *9*, 457.
- (12) (a) Takahashi, M.; Takechi, S. Evaluation of Chemically Amplified Resist Based on Adamantyl Methacrylate for 193 nm Lithography. *Proc. SPIE* **1995**, *2438*, 422. (b) Takechi, S.; Takahashi, M.; Kotachi, K.; Nozaki, K.; Yano, E.; Hanyu, I. A Novel Polymer for a 193 nm Resist. *J. Photopolym. Sci. Technol.* **1996**, *9*, 475.
- (13) Allen, R. D.; Wallraff, G. M.; DiPietro, R. A.; Hofer, D. C.; Kunz, R. R. 193 nm Single-Layer Positive Resists Building Etch Resistance Into a High-Resolution Imaging System. *Proc. SPIE* **1995**, *2438*, 474.
- (14) (a) Mathew, J. P.; Reinmuth, A.; Melia, J.; Swords, N.; Risse, W. (Eta(3)-Allyl)Palladium (II) and Palladium (II) Nitrile Catalysts for the Addition Polymerization of Norbornene Derivatives with Functional Groups. *Macromolecules* **1996**, *29*, 2744. (b) Safir, A. L.; Novak, B. M. Living 1,2-Olefin-Insertion Polymerizations Initiated by Palladium (II) Alkyl Complexes: Block Copolymers and a Route to Polyacetylene-Hydrocarbon Diblocks. *Macromolecules* **1995**, *28*, 5396.
- (15) (a) Goodall, B. L.; Benedikt, G. M.; McIntosh, L. H., III; Barnes, D. A. U.S. Patent 5 468 819, 1995 (to B. F. Goodrich Inc.). (b) Cherndron, H.; Brekner, M.-J.; Osan, F. Cycloolefin-Copolymere: Eine Neue Klasse Transparenter Thermoplaste Fortschritte in Der Polymer Synthese. *Angew. Makromol. Chem.* **1994**, *223*, 121. (c) Kaminsky, W. Olefinpolymerisation Mittels Metallocen Katalysatoren Fortschritte in Der Polymer-Synthese. *Angew. Makromol. Chem.* **1994**, *223*, 101.
- (16) Crivello, J. C.; Shim, S. Y. Chemically Amplified Electron-Beam Photoresists. *Chem. Mater.* **1996**, *8*, 376.
- (17) Houlihan, F. M.; Wallow, T. I.; Nalamasu, O.; Reichmanis, E. Synthesis of Cycloolefin-Maleic Anhydride Alternating Copolymers for 193 nm Imaging. *Macromolecules* **1997**, *30*, 6517. (b) Wallow, T. I.; Houlihan, F. M.; Nalamasu, O.; Chandross, E. A.

- Neenan, T. X.; Reichmanis, E. Evaluation of Cycloolefin-Maleic Anhydride Alternating Copolymers as Single-Layer Photoresists for 193 nm Lithography. *Proc. SPIE* **1996**, 2724, 355.
- (18) Potter, G. H.; Zutty, N. L. U.S. Patent 3 280 080, 1966.
- (19) Houlihan, F. M.; Wallow, T. I.; Timko, A. G.; Neria, S. E.; Hutton, R. S.; Cirelli, R. A.; Nalamasu, O.; Reichmanis, E. Recent Advances in 193 nm Single-Layer Photoresists Based on Alternating Copolymers of Cycloolefins. *Proc. SPIE* **1997**, 3049, 84. (b) Reichmanis, E.; Nalamasu, O.; Houlihan, F. M.; Wallow, T. I.; Timko, A. G.; Cirelli, R.; Dabbagh, G.; Hutton, R. S.; Novembre, A. E.; Smith, B. W. Resist Design Concepts for 193 nm Lithography: Opportunities for Innovation and Invention. *J. Vac. Sci. Technol., B* **1997**, 15 (6), 2528. (c) Houlihan, F. M.; Wallow, T. I.; Timko, A. G.; Neria, S. E.; Hutton, R. S.; Cirelli, R. A.; Kometani, J. M.; Nalamasu, O.; Reichmanis, E. A Commercially Viable 193 nm Single-Layer Resist Platform. *J. Photopolym. Sci. Technol.* **1997**, 10 (3), 511.
- (20) For an overview of diazonaphthoquinone resists see: Dammel, R. In *Diazonaphthoquinone-based Resist*; Shea, D., Ed.; SPIE Optical Engineering Press: Bellingham, WA, 1993; p 70.
- (21) (a) Reichmanis, E.; Wilkins, C. W., Jr.; Chandross, E. A. A Novel Approach to o-Nitrobenzyl Photochemistry for Resists. *J. Vac. Sci. Technol.* **1981**, 19 (4), 1338. (b) Wilkins, C. W., Jr.; Reichmanis, E.; Chandross, E. A. Lithographic Evaluation of an o-Nitrobenzyl Ester Based Deep-UV Resist System. *J. Electrochem. Soc.* **1982**, 129 (11), 2552.
- (22) (a) O'Brien, M. J. Novolac Based Photoresists Combining Chemical Amplification and Dissolution Inhibition. *Polym. Eng. Sci.* **1989**, 29, 846. (b) Crivello, J. V. Deep-UV Chemically Amplified Dissolution-Inhibited Photoresists. *Chem. Mater.* **1994**, 6, 2167.
- (23) Allen, R. D.; Opitz, J.; Larson, C. E.; Wallow, T. I.; DiPietro, R. A.; Breyta, G.; Sooriyakumaran, R.; Hofer, D. C. The Influence of Photoacid Structure on the Design and Performance of 193 nm Resists. *J. Photopolym. Sci. Technol.* **1997**, 10 (4), 503.
- (24) (a) MacDonald, S. A.; Clecak, N. J.; Wendt, H. R.; Willson, C. G.; Snyder, C. D.; Knors, C. J.; Deyoe, N. B.; Maltabes, J. G.; Morrow, J. R.; McGuire, A. E.; Holmes, S. J. Airborne Chemical Contamination of a Chemically Amplified Resist. *Proc. SPIE* **1991**, 1466, 2. (b) 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. Preliminary Lithographic Characteristics of an All-Organic Chemically Amplified Resist Formulation for Single-Layer Deep-UV Lithography. *Proc. SPIE* **1991**, 1466, 13. (c) MacDonald, S. A.; Hinsberg, W. D.; Wendt, R. H.; Clecak, N. J.; Willson, C. G.; Snyder, C. D. Airborne Contamination of a Chemically Amplified Resist. 1. Identification of Problems. *Chem. Mater.* **1993**, 5, 348. (d) Hinsberg, W. D.; MacDonald, S. A.; Clecak, N. J.; Snyder, C. D. Airborne Contamination of a Chemically Amplified Resist. 2. Effect of Polymer Film Properties on Contamination Rate. *Chem. Mater.* **1994**, 6, 481.
- (25) Asakawa, K.; Ushiroguchi, T.; Nakase, N. Effect of Basic Additives on Sensitivity and Diffusion of Acid in Chemical Amplification Resists. *Proc. SPIE* **1995**, 2438, 563.
- (26) (a) Houlihan, F. M.; Kometani, J. M.; Timko, A. G.; Hutton, R. S.; Cirelli, R. A.; Reichmanis, E.; Nalamasu, O.; Gabor, A. H.; Medina, A. N.; Biafore, J. J.; Slater, S. G. 193 nm Single-Layer Photoresists Based on Alternating Copolymers of Cycloolefins: The Use of Photogenerators of Sulfamic Acids. *Proc. SPIE* **1998**, 3333, 73. (b) Houlihan, F. M.; Kometani, J. M.; Timko, A. G.; Hutton, R. S.; Cirelli, R. A.; Reichmanis, E.; Nalamasu, O.; Gabor, A. H.; Medina, A. N.; Biafore, J. J.; Slater, S. G. Photogenerators of Sulfamic Acids: Use in Chemically Amplified Single-Layer Resists. *J. Photopolym. Sci. Technol.* **1998**, 11 (3), 419.

AR970150N