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Chemical Amplification in High-Resolution Imaging Systems

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The ready availability of inexpensive, high density semiconductor devices has made the "computer age" possible. These devices, which perform the central functions of computing, have shrunk dramatically over the past 20 years. Reduced circuit element size not only allows more transistors to be packed into a smaller volume but also reduces manufacturing costs. For example, today an aspiring graduate student can walk into the local computer discount store and, for about \$1000, purchase a credit card size package containing enough semiconductor memory to hold 16×10^6 characters (16 MB, enough to hold approximately 8000 double-spaced typewritten pages). In 1974, only 20 years ago, 16 MB of semiconductor memory would have occupied a volume of 224 L or slightly larger than a

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55-gal solvent drum. And while we do not know the exact selling price for this 16 MB, industrial historians recently estimated the manufacturing cost at \$144,000.¹

The photolithographic process used in microelectronics manufacturing defines the size of all circuit elements. Consequently, continued improvements in lithography have been essential to miniaturizing these components. The current photolithographic process^{2,3} outlined in Figure 1 is remarkably effective. As a result, large-scale manufacturing of the present generation of 16-Mbit dynamic random access memory (DRAM) chips with 0.5- μm features is possible using ultraviolet light from a mercury arc lamp.^{4,5} To put this 0.5- μm imaging achievement in proper perspective, recall that 0.5 μm (500 nm) is about the wavelength of visible light. Or, on a biological scale, these 0.5- μm structures are smaller than a typical bacterium (1–5 μm) but larger than the AIDS virus (0.11 μm). Continued progress in both microlithographic materials and techniques will play a central role in the development of more advanced devices containing even smaller structures.

To make a semiconductor device, a silicon wafer is coated with a 0.5–10 μm thick film of photoresponsive

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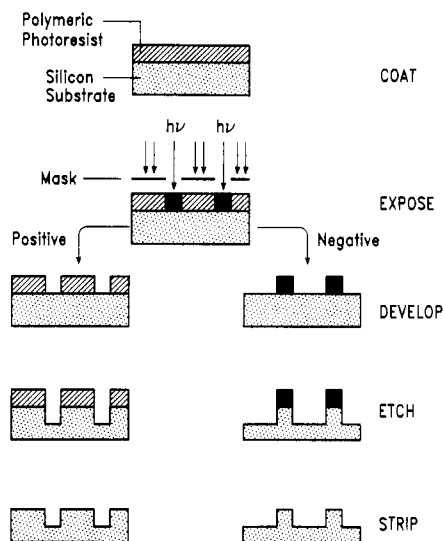


Figure 1. Outline of the general photolithographic process used to manufacture a semiconductor device.

polymer and exposed to UV light through a stencil called a mask. Radiation exposure alters the film's chemical structure in regions exposed to light. This chemical change produces differences in dissolution rate in appropriate solvents. Selective dissolution of either the exposed or the unexposed areas of the film produces positive or negative tone images, respectively.

The photolithographic process produces a three-dimensional relief image in the thin polymeric film that faithfully replicates the opaque and transparent areas of the mask. This polymeric relief image is subsequently transferred to the underlying substrate by a sequence of etching, deposition, or implantation steps to ultimately produce the active device.^{2,3}

While a variety of issues influence the resolution of the lithographic process, two major factors are the wavelength of ultraviolet light used in the exposure process and the nature of the photosensitive polymeric imaging layer (labeled "photoresist" in Figure 1). Traditional lithography equipment uses a high-pressure mercury arc lamp, emitting light in the range 250–450 nm, as a radiation source. In general, resolution improves as wavelength decreases. As a result, there has been a gradual shift from exposure at the major mercury emission lines (436, 404, or 365 nm) to the spectral region around 250 nm [commonly called deep UV (DUV)]. However, the increased resolution associated with using 250-nm light is accompanied by a substantial reduction in available UV flux because the 254-nm line is reabsorbed by other mercury atoms in the high-pressure Hg arc lamp. Therefore, to take practical advantage of the higher resolution offered by 250-nm lithography, one must develop either a brighter light source or a more sensitive resist that operates with far fewer photons. Excimer lasers provide an attractive solution to the problem of low photon flux, yet the complex optics of even the best systems severely decrease the light available for photochemistry.⁶ As a result, high-sensitivity resists are still required even with excimer lasers. One approach to high-sensitivity

resists is to design a photoinduced *catalytic* scheme that responds to 250-nm light. In this approach, termed *chemical amplification*, the initial radiochemical event produces a catalyst that initiates a chain reaction sequence that alters the solubility of the polymeric film.

In the early 1980s, our groups jointly developed the first chemically amplified resist system that responds to 254-nm light.^{7–10} These concepts were later used in the large-scale manufacture of 1-Mbit DRAMs¹¹ as well as 16-Mbit DRAMs^{4,12} and are also being used in the pilot line production of the 64-Mbit memory chip.¹³ This Account describes the versatile chemistry of imaging systems where the chain reaction sequence is acid catalyzed, and the acid catalyst is photochemically generated.

The "*t*-BOC Resist" System

Our first implementation of chemical amplification in deep-UV lithography made use of the well-known thermal cleavage of *tert*-butyl esters and carbonates.¹⁴ This thermal reaction normally occurs well above 150 °C, but in the presence of a trace of acid, the thermolysis temperature may be reduced to below 100 °C. However, in order to use this acid-catalyzed thermolysis for lithography, one must be able to photochemically generate acid. Fortunately, there are several photoactive compounds that liberate strong acid upon exposure to light.^{15–17} Therefore, the "*t*-BOC resist" system consists of a mixture of poly[4-[(*tert*-butyloxy-carbonyl)oxy]styrene] (PBOCST), a polymer with labile *tert*-butyl carbonate side groups, and triphenylsulfonium hexafluoroantimonate, a photoactive compound that generates strong acid. Figures 2 and 3 outline the mechanism of operation of this resist. Exposing the resist film through a mask (Figure 2) creates a latent image consisting of exposed areas with strong acid dispersed in the *tert*-butyl carbonate-containing polymer along with unchanged unexposed areas. Upon heating to 100 °C, the acid catalyzes the decomposition of the *t*-BOC groups with release of CO₂ and isobutylene (Figure 3), reducing the resist film thickness in the exposed areas, and modifying the chemical composition of the coating. Since this thermolysis is done at a low temperature, the unexposed areas of the film remain unaffected. Image development occurs readily because of the different chemical compositions of the exposed (phenolic) vs unexposed (carbonate) areas of the film. In fact, the resist is unusually versatile, providing both

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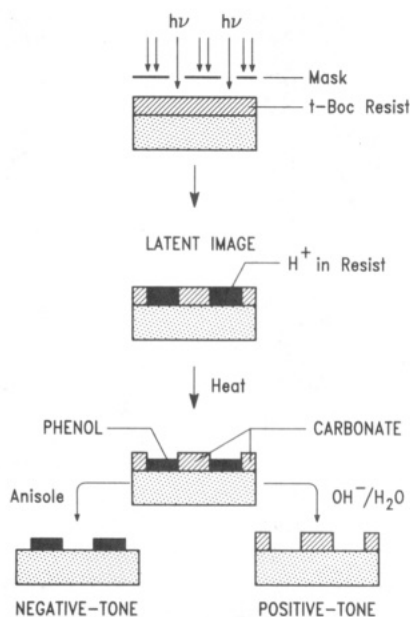


Figure 2. Lithographic sequence used to image the "t-BOC" resist system.

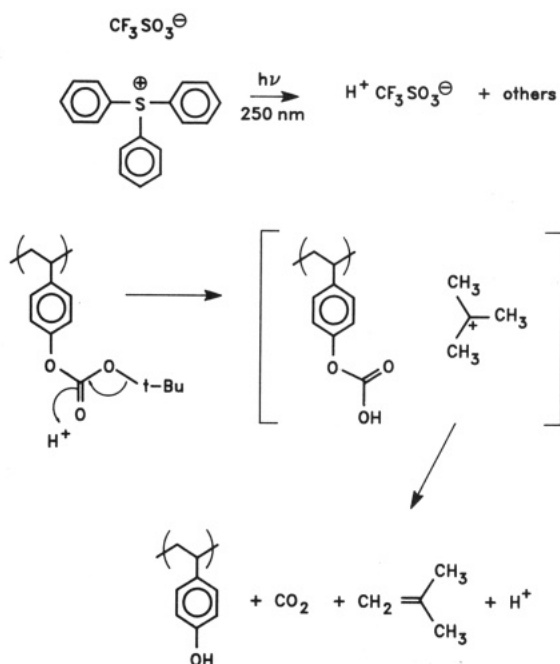


Figure 3. Acid-catalyzed decomposition of *tert*-butyl carbonate.

positive-tone imaging by development with aqueous base and negative-tone imaging with anisole as the developing solvent. Poly[4-[(*tert*-butyloxycarbonyl)oxy]styrene] is prepared¹⁸ by free radical polymerization of the corresponding styrenic monomer, which is obtained in two steps (Wittig reaction and reaction with di-*tert*-butyl dicarbonate) from a commercially available precursor, *p*-hydroxybenzaldehyde.

The mechanism shown in Figure 3 demonstrates the reason for chemical amplification. The initial protonation of the *t*-BOC group is followed by heating to a temperature that is high enough to provide the necessary activation energy for the acid-catalyzed cleavage step, but below that required for the uncatalyzed thermal cleavage. Cleavage of the carbonate results in

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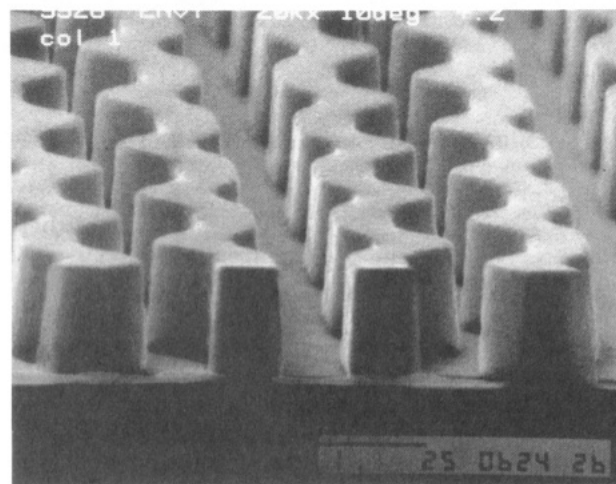


Figure 4. Scanning electron micrograph of 0.5- μm resist image printed with DUV lithography.

loss of carbon dioxide and recovery of a proton in the elimination step that releases isobutylene. As a result of chemical amplification, the radiation dose required to produce an image is very small compared to the dose required by conventional (nonamplified) resists. For example, the *t*-BOC resist used in the 1-Mbit DRAM program was processed at 0.9- μm dimensions with an exposure dose of only 1–2 mJ/cm². In contrast, classical novolac-diazonaphthoquinone photoresists³ require an exposure dose of between 200 and 300 mJ/cm² at 365 nm. An adaptation of the same catalytic scheme, using a copolymer of 4-hydroxystyrene and 4-[(*tert*-butyloxycarbonyl)oxy]styrene with an acid photogenerator, is now in commercial use. Figure 4 shows a scanning electron micrograph (SEM) of the 0.5- μm -wide relief image generated in the DUV resist system used in the current 16-Mbit program.

This basic catalytic design approach has been extended to several other imaging systems such that chemical amplification based on acid catalysis is now the predominant approach used to design modern resists for DUV, electron beam, or X-ray applications. This Account will focus on the system shown in Figures 2 and 3 as the *t*-BOC resist system is the "grandfather" of this whole new family of resists. This extended class of imaging systems has been recently reviewed elsewhere by several authors.^{19,20}

Can a Catalytic Process Preserve Image Resolution?

It is rather surprising that one can create high-resolution images from a catalytic system. It is reasonable to assume (before running the experiment) that the photogenerated acid produced in the exposed regions of the resist film would simply diffuse into the neighboring unexposed areas and destroy the image acuity. However, an early review paper²¹ on acid-catalyzed systems demonstrated that 1.0- μm images could be printed in a *tert*-butyl ester resist. Recently, submicron images have been resolved where the feature size is very close to the wavelength of the exposing light.

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Specifically, 0.25- μm images (250 nm) have been obtained in an acid-catalyzed system using 248-nm light,²² and images as small as 0.1 μm (100 nm) have been printed with 193-nm light.²³

The inherent resolution limit of the *t*-BOC resist system (Figure 2) was determined using a modified scanning transmission electron microscope (STEM) with a beam diameter of 2 nm.^{24,25} The small beam diameter gives the electron beam exposure system very high resolution. In this study, a 54-nm film of PBOCST yielded 40-nm-wide images when processed in the positive tone, and 19-nm-wide images when processed in the negative tone. These images were the smallest that could be printed and therefore appear to represent the current resolution limit of the resist system.²⁴ For comparison, the standard, high-resolution, noncatalytic electron beam resist, poly(methyl methacrylate) (PMMA), yields 15 nm minimum dimension images but requires a significantly higher exposure dose.^{3,24} While this important study clearly demonstrated the high resolution of an acid-catalyzed system, the result must be extrapolated to other systems very carefully. For example, the presence of residual casting solvent has been shown to increase the acid diffusion length,²⁶ and ¹⁴C radiotracer studies²⁷ have shown that the amount of residual solvent remaining in the film after coating varies widely as a function of polymer structure. These findings suggest that the rapid diffusion of the acid catalyst in some polymer matrices containing residual solvent may result in a significant loss of resolution.

Structural Design of Chemically Amplified Resists

Despite their excellent performance, there is nothing unique about *tert*-butyl carbonates for this imaging application. The key step in the cleavage reaction outlined in Figure 3 is the formation of a stabilized species, such as the *tert*-butyl carbocation, that can undergo elimination to regenerate the catalyst. The structural requirements for the reactive centers of the resist are therefore met by moieties that can lead to stabilized carbocations with at least one hydrogen atom located on an adjacent carbon. For example, resists containing pendant *tert*-butyl esters, rather than *tert*-butyl carbonates, though less effective than those containing *t*-BOC groups, can be used as chemically amplified materials.^{23,28} The difference in sensitivity between these related families is easily explained by considering the electronegativity of the added oxygen

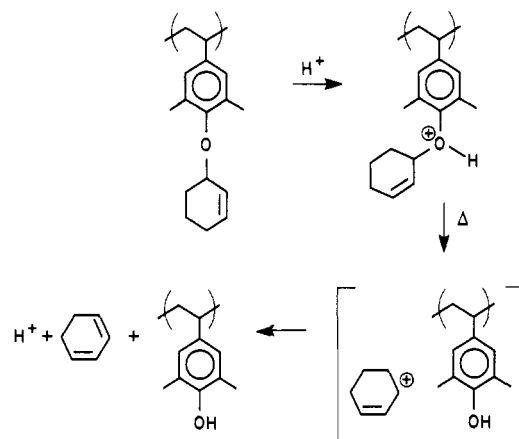


Figure 5. Acid-catalyzed decomposition of allylic ether.

substituent in the *tert*-butyl carbonate.^{14,29} Once the carbonyl group has been protonated, electron withdrawal facilitates the cleavage of the alkyl group.

The same type of cleavage reaction is also possible with polymers containing suitable ethers as pendant groups. Indeed, poly[4-(*tert*-butoxy)styrene] undergoes the same type of acid-catalyzed modification with formation of poly(4-hydroxystyrene) and isobutylene.³⁰⁻³² The concept is readily extended to other ethers^{30,31} that cleave to form stabilized carbocationic species that subsequently undergo elimination with regeneration of a proton. For example, Figure 5 shows the modification of a polymer containing a 2-cyclohexenyloxy pendant group by protonation of the ether oxygen followed by thermolysis of the cyclohexenyl group. The reaction proceeds easily because a stabilized allylic carbocationic intermediate is formed. This intermediate undergoes ready elimination with liberation of a proton, thereby ensuring that chemical amplification is achieved. Appropriately functionalized benzylic carbonate, ester, or ether substituents are also suitable.^{30,31} This is confirmed in a simple study of the thermolysis of several poly(alkyl 4-vinylbenzoates)²⁸ in which the alkyl groups are respectively *tert*-butyl, 2-cyclohexenyl, and 1-phenylethyl (Figure 6). All of these benzoates function as lithographic imaging systems when mixed with a photoacid generator, but the processing temperature must be adjusted to reflect the stability of the specific carbocationic intermediate that is generated during thermolysis. An analogous study, with similar conclusions, was conducted on a series of polymethacrylate alkyl esters.³³

The concepts outlined above, utilizing acid-labile carbonate, esters, or other similar groups, have been used in numerous other clever designs^{19,20,34-37} of chemically amplified resists. Examples of these sys-

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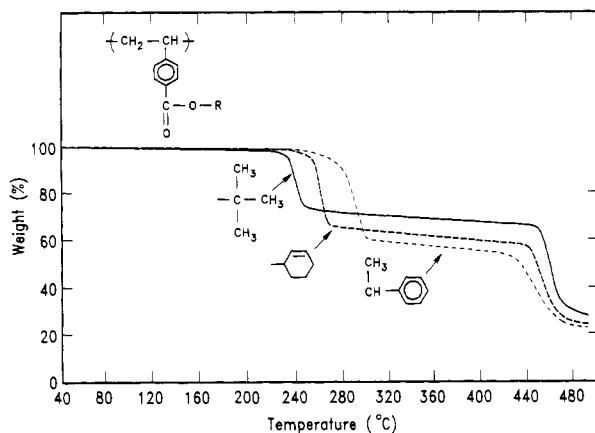


Figure 6. Thermogravimetric analysis of a side group ester series.

tems, shown in Figure 7, all incorporate polymers with a *tert*-butyloxy pendant group on the polymer side chain. As expected, these polymers all undergo a very large polarity change when the *tert*-butyl group is removed, allowing image development by differential dissolution as outlined above. Although all of these designs contain other features such as an increased glass transition temperature,³⁴ an enhanced cleavage mechanism,³⁵ or low optical absorbance in the UV,³⁷ their sensitivities remain high, requiring deep-UV exposure doses of 50 mJ/cm² or less.

Alternate Designs Using Multiple Main-Chain Scission

The cleavage of *tert*-butyl carbonates, esters, or ether groups need not be restricted to the polymer side chain. These groups may be used in the backbone of polymers, as acid-catalyzed cleavage processes occurring throughout the main chain of a polymer may also be exploited for imaging. In these backbone systems, the photogeneration of acid within the polymers, followed by heating to carry out *catalyzed* thermolysis, causes scission of the polymer main chain and a corresponding reduction in molecular weight. If the fragments resulting from main-chain cleavage are volatile, a relief image can be formed by simply heating the exposed film. If the fragments are not volatile, they can often be selectively dissolved in an appropriate solvent to yield a relief image. We have studied chemically amplified imaging materials based on polycarbonates,³⁸⁻⁴² polyethers,⁴³ and polyesters⁴⁴ that undergo this main-chain,

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acid-catalyzed thermolytic cleavage. Figure 8 shows examples of such systems, and Figure 9 demonstrates the imaging capability of an acid-labile polycarbonate that also operates with a low exposure dose.

Using Small Molecules as Dissolution Inhibitors

The previous sections have outlined approaches in which the acid-cleavable moiety was incorporated into the side chain or the main chain of polymers. A third approach, utilizing the same concept of acid-catalyzed thermolytic cleavage, makes use of a small organic molecule dispersed into a phenolic matrix resin.⁴⁵⁻⁴⁹ The phenolic resin itself dissolves rapidly in dilute aqueous base, but in the presence of a hydrophobic additive such as the *tert*-butyl carbonate of a bis(phenol),^{46,47} it dissolves at a much slower rate. Photogeneration of acid within a film containing both the phenolic polymer and the hydrophobic additive, followed by thermolysis, causes cleavage of the *tert*-butyl carbonate group from the additive, converting it into the bis(phenol), thereby greatly enhancing the solubility of the exposed areas of the film. This allows the selective dissolution of these exposed areas by simply immersing the film in dilute aqueous base to provide a positive-tone image. Figure 10 shows examples of monomeric dissolution inhibitors that function on the basis of acid-catalyzed thermolysis. An interesting extension of this approach involves using the *tert*-butyl-substituted triarylsulfonium salt⁴⁹ shown at the bottom of Figure 10. This compound functions both as a photoacid generator and as a monomeric dissolution inhibitor.

Plasma Development

In traditional lithography, as outlined in Figure 1, the photosensitive organic film is exposed through a mask to UV light and then developed with solvent to yield a relief image. Recent work has shown that it is possible to develop the relief image with an oxygen plasma. Oxygen plasma processing of resist materials is complex, and a full description is beyond the scope of this Account.⁵⁰ Simplistically, one can view oxygen etching as providing an oxidative vacuum environment. Oxygen plasma rapidly converts organic films into volatile carbon oxides and water that are swept into the vacuum system. Other elements such as silicon, tin, or germanium are also oxidized in this environment, but their oxides are nonvolatile and hence remain on the surface of the film. Given these two observations, the current approach to designing plasma-developable resists involves introducing silicon into selected regions of an organic film.⁵¹ When such a film is placed into an oxygen plasma, the areas lacking silicon are removed

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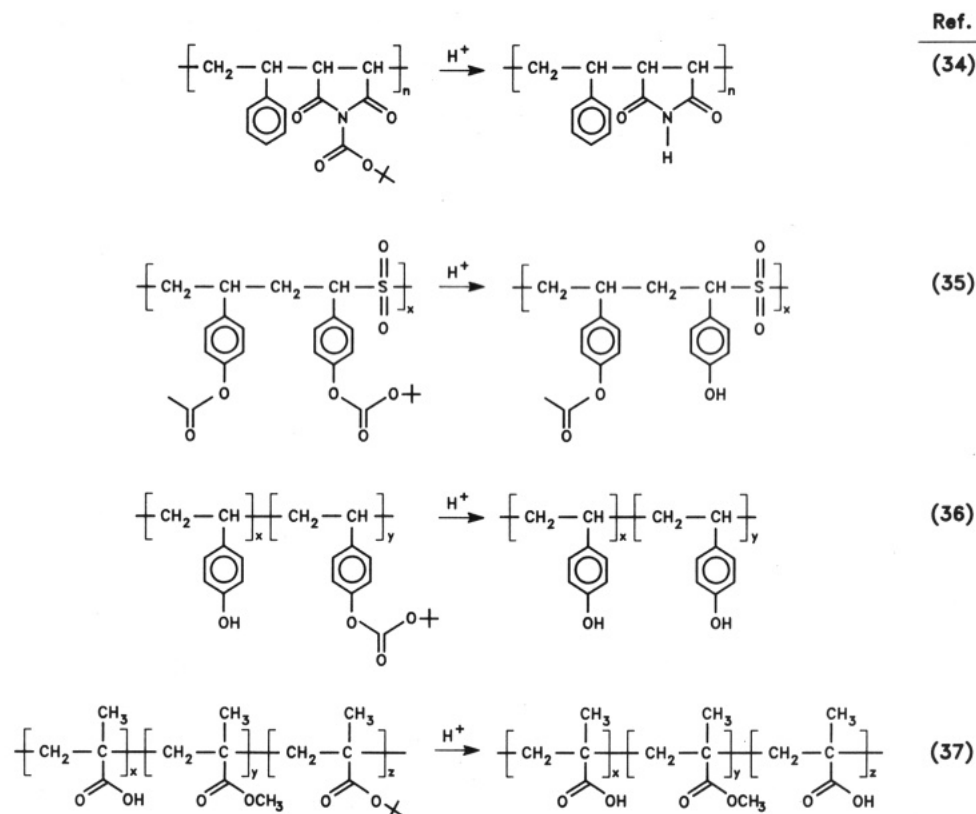


Figure 7. Examples of acid-catalyzed imaging systems containing a *tert*-butyloxy pendant group on the polymer side chain.

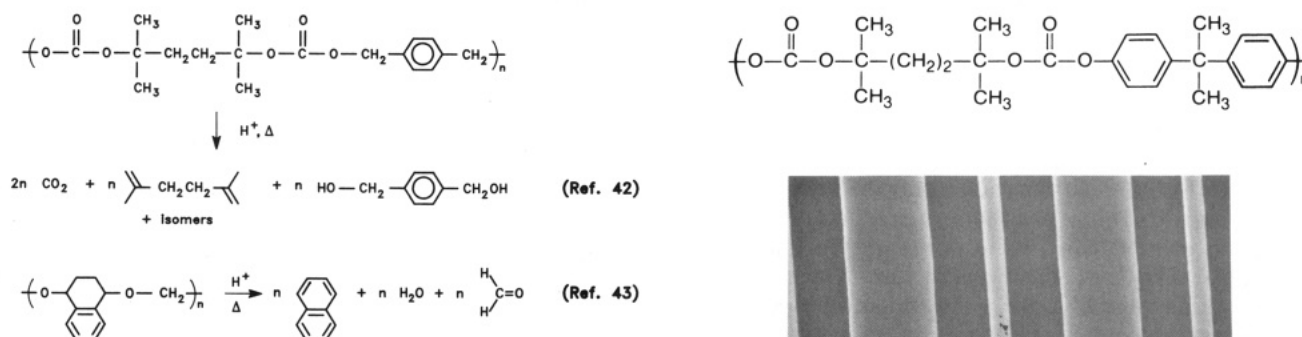


Figure 8. Examples of acid-catalyzed imaging systems based on multiple main-chain scission.

while regions containing silicon remain on the substrate. A thin film of refractory SiO₂ forms rapidly on the surface of the silicon-containing areas of the film. This thin oxide film protects the underlying material from further oxidation by the plasma.

The *t*-BOC resist system can be developed with an oxygen plasma if the exposed and baked film is treated with a silylating reagent such as hexamethyldisilazane (HMDS) or (trimethylsilyl)dimethylamine.⁵¹ This process is often carried out in the gas phase using silylating agent vapor to modify the polymer film. HMDS reacts with phenolic hydroxyl groups to form a silyl ether, but does not react with *tert*-butyl carbonates. Silicon is thereby selectively and covalently incorporated into only the exposed regions of the film. Oxygen plasma development yields a negative-tone image as outlined in Figure 11. This area-selective formation of silyl ethers has been confirmed by IR spectroscopy and Rutherford backscattering (RBS).⁵¹ Since HMDS also reacts with carboxylic acids, the same silylation/plasma development scheme can be used with

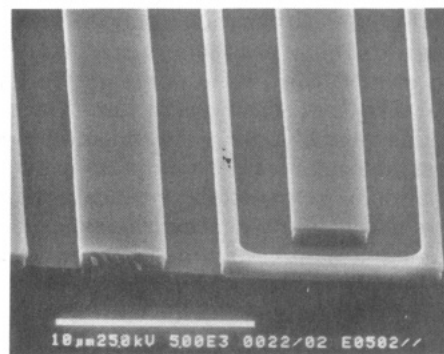


Figure 9. Scanning electron micrograph of the relief image generated by a main-chain polycarbonate.

other systems including poly(*tert*-butyl methacrylate)⁵¹ or poly(*tert*-butyl vinylbenzoate).⁵²

The negative-tone plasma development scheme shown in Figure 11 can be modified to yield a positive-tone image.⁵³ In this "image reversal process", the phenolic hydroxyl groups produced by the image exposure and baking are first reacted with methyl isocyanate vapor to form a methyl carbamate. Subsequent flood exposure and baking converts the remaining unexposed, and therefore unreacted, *tert*-butyl carbonates to phenolic hydroxyl groups. Finally, treatment with HMDS vapor selectively incorporates silicon into the areas that were

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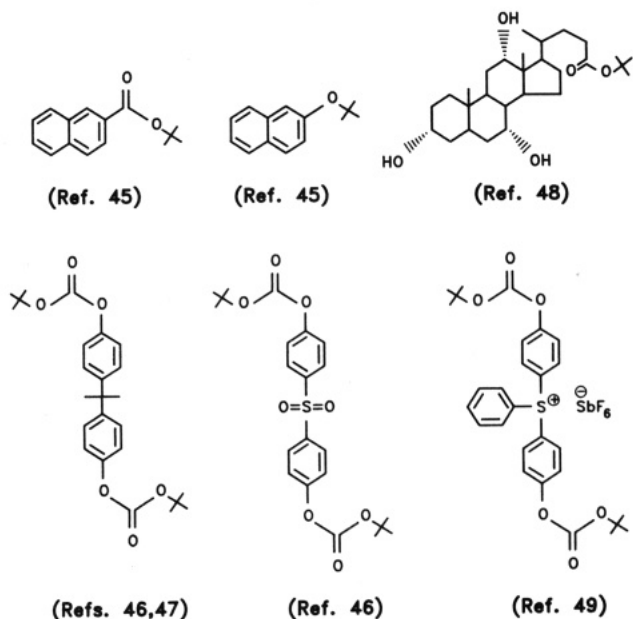


Figure 10. Examples of small molecule dissolution inhibitors that incorporate a *tert*-butyloxy group.

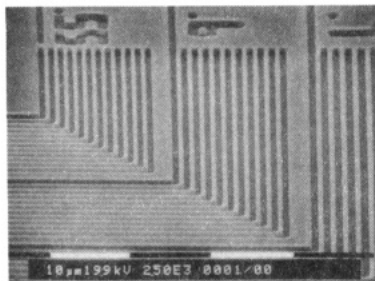
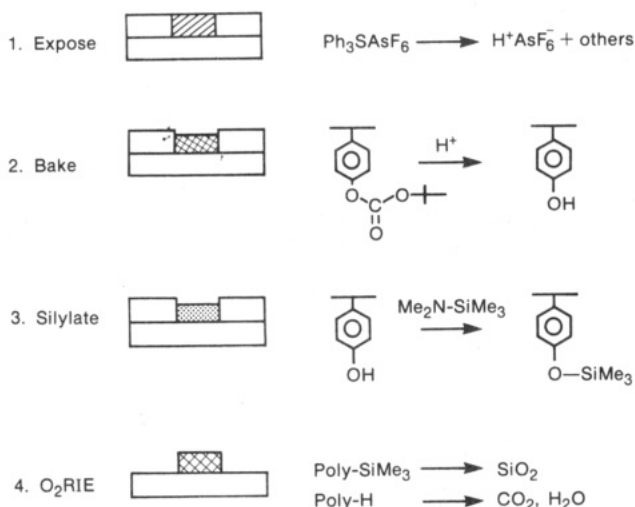


Figure 11. Negative-tone dry develop process: Outline of plasma-developable resist scheme based on silylating the resist after exposure to UV light.

not exposed during the imaging exposure. When a film processed in this way is placed into an oxygen plasma, the carbamate regions etch rapidly, yielding a positive-tone image. Two key features underlie this approach to plasma-developable resists. The first is photochemical generation of reactive functional groups within a polymeric film, and the second is the reaction of these functional groups with the proper organometallic reagent to induce oxygen plasma etch resistance.

Silicon, or any other element that forms a refractory oxide, may be employed to create an oxygen etch barrier.

Poisoning of the Photogenerated Acid Catalyst

The catalytic chain length of the *t*-BOC resist system (Figure 3) is quite large, approximately 1000 carbonate unit cleavages per proton.⁵⁴ This value for *tert*-butyl carbonate cleavage was studied as a function of photoacid generator structure, and it was found to range from a few hundred carbonate units per proton to several thousand units per proton⁵⁵ depending on the photogenerated acid. This long catalytic chain is precisely the feature that enables the *t*-BOC family of resists to operate with a small exposure dose. However, the long catalytic cycle also makes these systems vulnerable to "poisoning" by basic compounds. Furthermore, since the desired reaction in Figure 3 involves protonation of a weak base (the carbonate group), a wide range of weakly basic compounds competes effectively with the ester or carbonate oxygens for the photogenerated acid catalyst, poisoning the reaction.

Catalyst poisoning^{56,57} is a major problem for acid-catalyzed resist systems. Degradation of lithographic performance can occur if *t*-BOC resist coated wafers are allowed to stand for only a few minutes in air containing as little as a few parts per billion (ppb) of organic base.⁵⁷ Unfortunately, semiconductor device manufacturing uses many materials that generate volatile base: tetramethylammonium hydroxide developer solutions, hexamethyldisilazane adhesion promoters, and *N*-methylpyrrolidone (NMP) strippers are typical examples. In addition, common cleaning solutions, paints, and construction materials often contain volatile amines.⁵⁷ As a result, the air in semiconductor manufacturing areas is often contaminated with extremely low levels of amine vapor. Although these levels are well below federal standards (OSHA), they are sufficient to preclude the use of acid-catalyzed resists unless the resist is completely isolated from the workplace environment. Presently, two general isolation methods are used: (1) handling and storing coated wafers in air that has been filtered through a high-efficiency activated carbon filter,⁵⁷ and (2) applying a protective polymer film directly on top of the resist^{56,58} immediately after resist application.

The rate at which a film of the *t*-BOC resist absorbs NMP from an airstream containing 10 ppb of [¹⁴C]-NMP has been quantified radiochemically.⁵⁷ This study demonstrated that the diffusion of NMP into the film is Fickian, and that the molar amount of NMP absorbed at the resist surface is on the same scale as the amount of photogenerated acid produced under typical conditions. A subsequent radioisotope study using two dozen different polymeric films found that

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NMP uptake varies with film structure and properties.⁵⁹ It was proposed that the *rate* of NMP incorporation at constant concentration would be minimized if the film was heated above T_g (thermal annealing to reduce free volume) and the *equilibrium concentration* could be reduced if the solubility parameter of the polymer differed significantly from that of NMP.⁵⁹ This very encouraging study suggests that it is possible to rationally design acid-catalyzed resist systems that will not absorb "damaging concentrations" of airborne contaminants and should therefore be stable to the low levels of amine found in typical manufacturing environments.

In another study, poly[[*tert*-butyloxycarbonyl]oxy]-styrene] was used to test the thermal annealing aspect of this theory. The meta and para isomers of this polymer have glass transition temperatures of 90 and 135 °C, respectively. If both films are baked at 100 °C (above T_g for meta but below T_g for para), the meta isomer exhibits far greater stability than the para isomer toward airborne contamination. This result is fully consistent with thermal annealing of the meta film and consequent reduced diffusion rate, relative to that of the para film.²²

In reality, parts per billion level amine contaminated air is commonplace, and the harmful effect this contamination has on acid-catalyzed resist systems has motivated several research groups to pursue solutions to the problem. A more satisfying alternative to high-efficiency air filtration or an overcoat layer is to devise new chemically amplified resists specifically designed

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to be insensitive to airborne basic contaminants. The trends observed in the [¹⁴C]NMP absorption study provide guidance for the search for such new systems, and rapid progress is being made.

Concluding Remarks

Incorporating chemical amplification into the design of resist materials has opened a new avenue for high-resolution imaging and has contributed to the development of better and more powerful microelectronic devices. This Account demonstrates the classical interplay of basic and applied research, where coupling a fundamental understanding of reaction mechanisms to simple resist design strategies has led to materials with very practical applications. In its early days, the "t-BOC resist" was considered by many to be just an interesting laboratory curiosity, perhaps because it was too different from traditional resists to be taken seriously. The synergistic work of dedicated scientists and engineers in industry and academia has transformed this "curiosity material" into several generations of practical resists used to make millions of state-of-the-art computer chips and opened the door to new approaches to design the next generation of resist materials.

The authors acknowledge the important contributions of their numerous co-workers at IBM, the University of Ottawa, and Cornell University whose names are cited in the list of references. In addition, we thank the dedicated processing engineers of IBM Burlington and East Fishkill who implemented these chemically amplified DUV resists on the manufacturing floor. Finally, we thank Jody Hucko for her insightful editorial comments.