

Organic imaging materials: a view of the future

Michael D. Stewart,¹ Kyle Patterson,² Mark H. Somervell¹ and C. Grant Willson^{1,2*}

¹Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, USA

²Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, USA

Received 15 May 2000; accepted 22 August 2000

ABSTRACT: Over the last half century, the world semiconductor industry has provided phenomenal increases in computing power while simultaneously lowering production costs. This achievement is largely the result of the industry being able to print smaller and smaller features using photolithographic techniques. The organic imaging materials used in the photolithography (generally known as photoresists) have undergone many changes over the industry's history, and if the increases in computing speeds and decreases in costs are to continue in the future, more changes are necessary. This paper discusses the current generation of photoresists and the on-going development of future generation photoresist technologies. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: organic imaging materials; photoresists; lithography; thin-layer imaging

INTRODUCTION

Tremendous economic growth has been made possible by the availability of cheap and powerful semiconductor devices. Microchips are now an integral part of a great variety of devices ranging from the mundane to exotic, from wristwatches and cars to satellites and cruise missiles. And, of course, the explosive growth of the Internet would never have been possible without the semiconductor industry's ability continuously to provide more computing power at lower prices. As an example of the industry's ability to improve performance while lowering costs, one can look at the change in computer memory chips prices over the last decade. In 1993, \$1000 would buy 16 megabytes of computer memory; today, almost 1000 megabytes can be purchased for the same amount. As another measure of the tremendous value provided by the semiconductor industry, it should be noted that the cost of a single transistor in an advanced microprocessor such as AMD's Athlon chip is of the same order of magnitude as the cost of a single printed word in Austin's local newspaper, the *Austin-American Statesman* (based on a \$200 Athlon processor with 22 million transistors¹ and *Austin-American Statesman* at weekday price of 50¢ with average 1600 words per page and 80 pages)

The improvement in performance and price of microelectronic devices is mainly the result of the continual shrinkage in the minimum feature dimension

that can be produced on a silicon wafer. Since wafer-processing time is essentially independent of feature dimension, printing smaller features allows greater numbers of devices to be printed on a wafer in the same amount of time, thus decreasing device-manufacturing costs (at least on a per transistor basis). In addition to improving manufacturing yields, smaller feature sizes also improve computing speed by decreasing the travel distance of electrical signals in the device.

There are many different steps necessary for the construction of an integrated circuit device, but it is the photolithographic step that limits the minimum printable feature size. A schematic of the photolithographic process is presented in Fig. 1. In this process a photomask, which contains a stencil representation of a device layer, is used to selectively block the transmission of exposure radiation. The light passing through the photomask is collected by a series of lenses and then projected on to a silicon wafer coated with a light-sensitive material known as a photoresist. The photoresist undergoes a photochemical reaction that changes its solubility in developer solution. Treatment with a developer solvent produces a three-dimensional relief image of the photomask pattern on the silicon substrate. Depending on whether exposure enhances or inhibits photoresist dissolution, the image may be in either positive or negative tone. The relief image created by photolithography provides patterned access to the underlying substrate and can be used as a mask for other processing steps such as etching, ion implantation or metal deposition that transfer some aspect of the circuit pattern into the underlying substrate. Typical integrated circuit designs require 10–25 different precisely pat-

*Correspondence to: C. G. Willson, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, USA.

E-mail: willson@che.utexas.edu

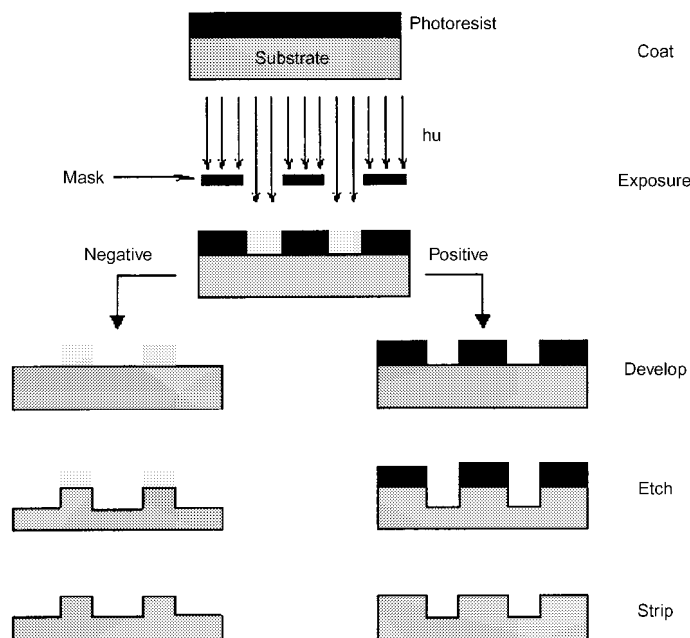


Figure 1. The photolithographic process. (1) Substrate is coated with photoresist. (2) Exposure through a mask generates a latent image in the photoresist. (3) Development removes soluble regions, in a positive tone system exposed regions become soluble. (4) Image is transferred into substrate with an etch process. (5) Any remaining photoresist is removed

terned layers, stacked one upon the other, to create a functional device.

Several factors influence the minimum feature size printable by photolithographic techniques, two of the most important being the wavelength of the exposure radiation and the numerical aperture of the projection lens system. According to the Rayleigh relation:

$$R \propto \lambda/NA$$

the resolution (R) of photolithographic process is proportional to the exposing wavelength (λ) and inversely proportional to the numerical aperture (NA). Industry has pursued, and continues to pursue, changes in both variables as pathways to smaller features, but this paper will concentrate on the development of organic imaging materials needed for shorter and shorter exposure wavelengths.

Production of the most advanced commercially available microdevices is currently being carried out in the deep ultraviolet (DUV) region at a 248 nm exposure wavelength, which corresponds to the output of a krypton–fluorine (KrF) excimer laser. Features smaller than 180 nm are being produced using this wavelength. In the near future the industry will seek to improve resolution by changing to photolithography based on the 193 nm light generated by argon–fluorine (ArF) excimer lasers. This wavelength is expected to allow production of devices with features down to at least 130 nm. Production of 100 nm and sub-100 nm devices is expected to require another wavelength decrease down to 157 nm exposure (fluorine excimer laser).

Each of these changes in exposure wavelength has unfortunately required the development of new organic imaging materials. Materials designed for 248 nm are too strongly absorbing at 193 nm to allow proper imaging, and likewise materials designed for 193 nm are too opaque at 157 nm to image properly. This paper describes the development and design of the current generation 248 and 193 nm photoresist materials and the progress towards the development of a photoresist for 157 nm microlithography. A historical account of photoresist development prior to DUV resists can be found in several references.^{2–5}

PHOTORESISTS FOR KrF LITHOGRAPHY

At the time when the switch to the 248 nm wavelength was first contemplated, the output intensity of available exposure sources at 248 nm was about an order of magnitude lower than what was in use for imaging at higher wavelengths. The diazoquinone novolac photoresists⁴ in use at that time lacked the radiation sensitivity to be useful with the high-pressure mercury, DUV lamp sources then available. Unless brighter DUV sources could be developed, a more sensitive resist system would be required. Brighter sources were eventually developed in the form of excimer lasers, but it was found that high-sensitivity resists were still required because high-intensity laser pulses tend to damage and degrade the expensive imaging optics of the production equipment.^{6,7}

One approach to designing a higher sensitivity resist system is to use the principle of ‘chemical amplification.’

In a chemically amplified system, exposure photons do not directly cause a solubility switching reaction event; rather, they are used to generate a stable catalytic species. The photogenerated catalyst then initiates a chain reaction or promotes a cascade of reactions that changes resist solubility in exposed regions. The apparent quantum efficiency for the solubility switching reaction in such a resist system is the product of the quantum efficiency for catalyst generation and the catalytic chain length. Catalytic chain lengths in the many hundreds are common, so in effect the apparent quantum efficiency can be very much greater than unity. One photochemical conversion can cause several chemical reactions, and thus the exposure can be said to have been 'chemically amplified.'

The first chemically amplified systems for DUV photolithography were designed in the early 1980s.^{8–11} These resist systems were based on the phenolic polymer poly(4-hydroxystyrene) (PHOST) and its *tert*-butyl carbonate (t-BOC) protected analog poly(4-*tert*-butyloxycarbonyloxystyrene) (PTBOC). The principles behind this design have been used in the development of almost all subsequent photoresists. In this first system imaging contrast was provided by the difference in dissolution rate of the t-BOC-protected polymer and the unprotected polymer in certain solvents. By changing developer solvents the system could be imaged in either positive or negative tone. For example, in an aqueous base developer the protecting group slows dissolution allowing for positive tone imaging, whereas a solvent such as anisole gives negative tone imaging.

Imaging in this system occurs by selectively removing protecting groups in exposed regions to modulate solubility. This deprotection is accomplished by exploiting the acid-catalyzed thermolysis of the t-BOC group (Fig. 2). Upon DUV exposure, catalytic amounts of acid are generated from a photoacid generator (PAG) dispersed in the polymer matrix. Exposure creates a latent image of acid and a 1–2 min bake around a temperature of 100°C is required for the actual deprotection reaction to occur. The PAGs used in this system can be any one of several onium salts, first reported by Crivello and Lam in the late 1970s¹² and just recently reviewed.¹³ The catalytic chain length of in this 't-BOC' resist is extremely long, and can therefore be imaged at doses two order magnitudes lower than any previous systems.¹⁴

Chemical amplification solves the sensitivity problem, but it can cause other problems. For example, a catalyst that is mobile enough to promote several hundred reactions could possibly move from exposed regions into unexposed regions and cause loss of resolution. The acid catalyst, with its long catalytic chain length, is also susceptible to poisoning by base contaminants gettered from the atmosphere.

The migration of the catalyst into unexposed regions has never been the problem it was expected to be.

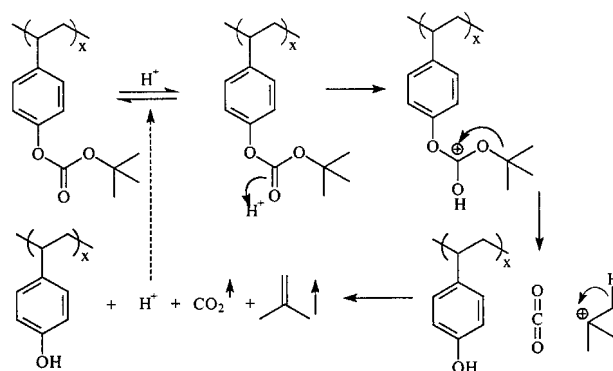


Figure 2. Mechanism of acid-catalyzed deprotection in tBOC resist system

Catalytic systems were initially met with great skepticism. Many people expected that the resolution in chemically amplified resists would be very poor, but this has not proven to be the case. Studies using extremely fine (2 nm) electron beam exposures have shown that the ultimate resolution of the t-BOC resist system is about 40 nm when processed in positive tone.^{15,16} Other studies have shown that line-width spread by catalyst migration is somewhat self-limiting.^{17,18} The reported self-limiting nature of linewidth spread has led to debate about the actual mechanisms responsible for acid diffusion/transport in chemical amplified resist systems.^{17–21}

The catalyst migration problem that was once expected to limit the usefulness of chemically amplified photoresists has, so far, not turned out to be a significant problem, but the largely unforeseen problem of atmospheric base contamination turned out to be very significant. Even in the controlled atmosphere of a cleanroom with atmospheric base levels of parts per billion, contamination caused unacceptable processing variations in early t-BOC-based systems.^{22,23} Atmospheric base contamination can also cause the more dramatic 'T-topping' effect (Fig. 3) when the acid generated in the resist's top layer is neutralized by contamination, preventing full deprotection at the resist–air interface. These contamination problems made it

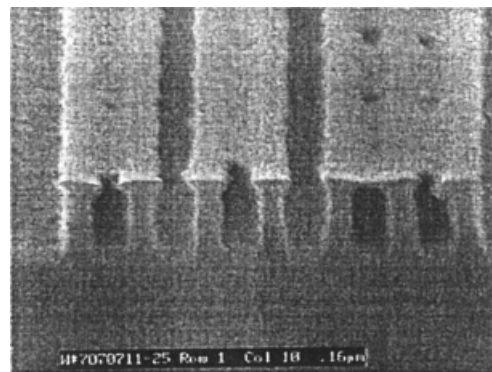


Figure 3. SEM micrograph showing 'T-topping' effect

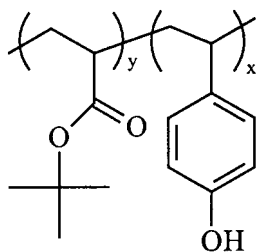


Figure 4. Structure of an ESCAP photoresist

necessary to isolate resist-coated wafers from the regular cleanroom atmosphere and protect them with expensive filter and containment systems.

Another way to avoid 'T-topping' is to tailor the background dissolution rate of the unexposed resist. In effect by giving the matrix resin a finite dissolution rate, the base-contaminated layer, which would normally cause the 'T-topping,' can just be dissolved away during development. The improvement in environmental stability more than compensates for small losses in resist thickness. The first resist system to incorporate a tailored background dissolution rate to improve environmental stability was IBM's APEX resist, which is simply a random copolymer of PHOST and PTBOC.

These problems with atmospheric contamination caused several groups to begin development of new photoresists that would be less sensitive to their surroundings. The ESCAP resist (Fig. 4) developed in the early 1990s was one particularly successful approach to lessening environmental sensitivity.^{24,25} Incorporation of *tert*-butyl acrylate to replace *tert*-butyloxycarbonyloxystyrene gave the resist a thermal decomposition temperature above its glass transition temperature (T_g). With a T_g below their thermal decomposition temperature, the ESCAP-class resists can be annealed above their T_g after spin coating to remove excess free volume and densify the film. Removing free volume improves environmental stability by lowering the diffusion rate of contaminants into the film. Previous systems thermally decomposed prior to reaching T_g so no above- T_g annealing was possible. Changing to *tert*-butyl acrylate also improved environmental stability by lowering the solubility of base contaminants in the resist film.

PHOTORESISTS FOR ArF LITHOGRAPHY

The continuous drive for higher resolution means that eventually 248 nm lithography will be unable to meet the semiconductor industry's requirement for smaller features. The switch to a shorter wavelength is in fact quickly approaching, with the first 193 nm production expected to begin this year. To make this switch possible, an entirely new group of photoresist materials had to be developed since all KrF resists are too strongly absorbing at 193 nm to permit proper imaging. Along with meeting

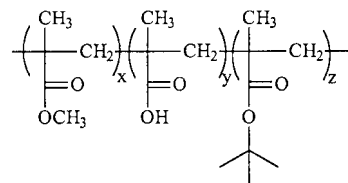


Figure 5. IBM version 1 acrylic-based 193 nm terpolymer

optical transparency requirements, new 193 nm photoresists must meet basic photoresist requirements, such as sensitivity, dry (plasma) etch resistance, substrate adhesion and acceptable mechanical properties. Economic factors, such as ease of synthesis, monomer cost and compatibility with industry standard developers and solvents are also important considerations.

The key difficulty in 193 nm photoresist design was the apparent inability to meet plasma etch resistance requirements while simultaneously meeting optical transparency requirements. Early in the development of 193 nm photoresists it was thought that in fact the two were going to be mutually exclusive. Dry etch resistance was thought to require incorporation of aromatic groups into the polymer, but most aromatics absorb strongly in the spectral region near 193 nm due to π - π^* transitions and, therefore, cannot be used in 193 nm photoresists. Fortunately, thanks to the work of Goken *et al.*,²⁶ it was empirically shown that aromaticity was not the controlling factor in determining etch resistance, rather it was simply the carbon-to-hydrogen ratio of the resist matrix that affected etch performance. Aromatics provide a convenient way to give a high C/H ratio, but they are not the only way.

Early development of 193 nm resists centered on acrylic-based polymers.^{27,28} The chemical amplification in acrylic systems, such as that shown in Fig. 5, is provided by acid-labile *tert*-butyl ester protecting groups which, upon exposure to photogenerated acid, cleave to produce base-soluble carboxylic acids. These systems have good optical transparency and imaging performance, but lack sufficient etch resistance owing to a low C/H ratio. Researchers at Fujitsu first reported that etch resistance of acrylic systems could be increased by incorporation of pendant alicyclic (polycyclic aliphatic) units into the polymer system.²⁹ Alicyclic units such as norbornane or adamantane achieve a high C/H ratios through incorporation of multiple rings rather than multiple carbon-carbon bonds that might absorb strongly at 193 nm. Researchers at IBM used the alicyclic pendant group concept to improve the etch resistance of their acrylic terpolymer system (IBM Version 1) by adding a fourth monomer, isobornyl methacrylate. This new tetrapolymer along with a steroid-based additive that improved dissolution properties and etch resistance comprised the IBM Version 2 photoresist platform³⁰ (Fig. 6). A wide variety of 'derivative' photoresist designs have been developed based upon acrylate matrix

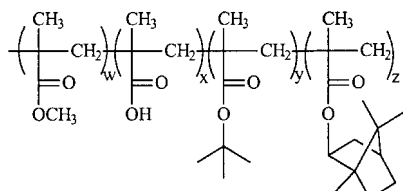


Figure 6. IBM version 2 acrylic-based 193 nm photoresist. Isobornyl methacrylate unit has been added to improve etch resistance

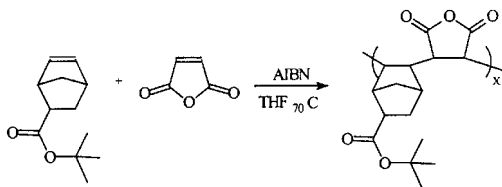


Figure 7. Synthesis and structure of alternating copolymer BNC-*alt*-MA, 193 nm photoresist

resins containing pendant alicyclic groups by other research groups.^{31–33}

These acrylic systems offer high-resolution imaging, but they have less than ideal etch resistance despite incorporation of alicyclic pendant groups. In KrF photoresists each monomer unit contains an etch-resistant aromatic unit, whereas in the ArF acrylic systems only a fraction of monomer units have an etch resistant pendant group. With such a limitation, it is fundamentally difficult for an acrylic resist to match the etch performance of a KrF system. To address this shortcoming, our research group began to study methods for creating polymers directly from cycloolefins which would incorporate an etch-resistant alicyclic structure in to the repeating unit.

Three basic methods of cycloolefin polymerization were identified as potential routes for synthesizing photoresist matrix resins: vinyl addition polymerization, ring-opening metathesis polymerization (ROMP), and free radical polymerization. Several polymers based on norbornene and norbornene derivatives were synthesized via these routes and were evaluated as potential resist materials.^{34–37} The most promising of these polymers, shown in Fig. 7, was an alternating copolymer of *tert*-butyl norbornene-5-carboxylate (BNC) and maleic anhydride (MA) prepared by free radical polymerization. The

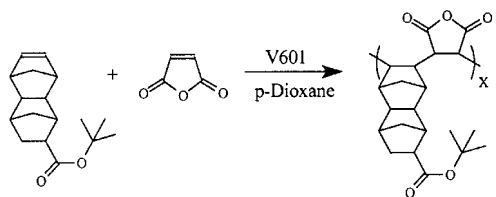


Figure 8. Synthesis and structure of alternating copolymer DBNC-*alt*-MA, 193 nm photoresist

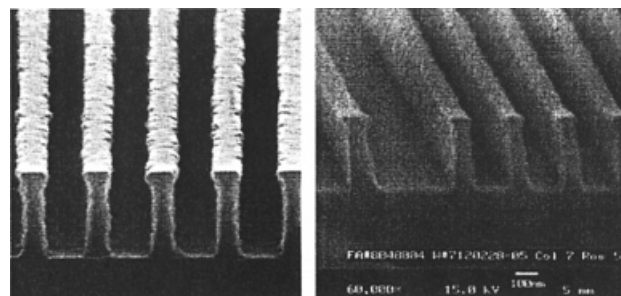


Figure 9. SEM micrograph of resist features printed at 193 nm. Left: 120 nm wide lines printed using binary photomask. Right: 80 nm wide lines printed using a 'phase-shifting' photomask

etch performance of this polymer was still not completely adequate, but a pathway to improve resistance was readily available. The C/H ratio was raised by switching from the norbornene monomer to its dinorbornene analog. *tert*-Butyl tetracyclo[4.4.0.1^{2,5}.1^{7,12}]dodec-3-ene-5-carboxylate (DBNC) was found to undergo alternating copolymerization with MA in a fashion very similar to BNC (Fig. 8). This polymer, when formulated with a photoacid generator, a cholate-based dissolution inhibitor, and a small amount of base additive, has imaged features down to 110 nm using a binary photomask. When used with a 'phase-shifting' photomask, features as small as 80 nm were printed.³⁶ Figure 9 shows scanning electron micrographs of resist features produced using this 193 nm system. A number of improvements and refinements in this basic resist design have been reported,^{38,39} and it is likely that commercial photoresists based on derivatives of this basic system design will support 193 nm production.

PHOTORESISTS FOR 157 nm PHOTOLITHOGRAPHY

Optical lithography with 193 nm light is expected to allow the production of devices with features dimensions down to near 100 nm. The production of 100 nm and sub-100 nm devices will likely require a different technology. In the past year the extension of optical lithography down to the 157 nm exposure wavelength has emerged as the semiconductor industry's favored successor to 193 nm lithography.⁴⁰ So-called 'next generation' lithography technologies based on electron beam projection lithography, ion beam projection lithography or x-ray lithography are seen as immature technologies, unlikely to be fully ready by 2005 when 100 nm size devices are expected to enter volume production. Optical lithography with 157 nm light offers the industry the chance to build upon decades of accumulated experience with optical techniques, while a switch to a 'next generation' technology would require a radical change in manufacturing processes and could be potentially disruptive.

Perhaps 157 nm lithography is not a radical departure from current lithographic techniques, but the technological challenges to its implementation are still formidable and its problems are compounded by an extremely short development schedule. Along with new photoresist materials (including casting solvents), new materials for lens systems and photomask substrates must be developed.

The challenge of designing a low-absorbance chemically amplified photoresist for 157 nm is complicated by a general lack of absorbance data for materials at such short wavelengths. The available information is not particularly reassuring; for example, water vapor is known to have extremely strong absorbance at 157 nm. This implies that the entire exposure beam path must be sealed against the atmosphere or purged with an inert gas—both complicated engineering tasks. It has also been reported that the absorbance of polyethylene is strong in the 157 nm spectral region.⁴¹ If the methylene units that comprise polyethylene absorb strongly, then polymers with methylene linkages for backbones, such as polyacrylates, polystyrenes and polynorbornenes, are also likely to absorb 157 nm light strongly. Researchers at MIT Lincoln Laboratories are currently surveying polymer materials with the aim of determining possible alternative backbone structures. Their work has shown that the transparency of polyethylene can be improved by appropriate placement of electron-withdrawing groups, such as fluorine and oxygen, into the polymer structure. Poly(vinyl alcohol), which incorporates electron-withdrawing hydroxyl groups on alternating carbons of a polyethylene backbone, absorbs less strongly than polyethylene. Highly-fluorinated analogs of polyethylene also have much improved transparency. The MIT group has also shown that silicon-based polymers, such as siloxanes and silesquioxanes, have high transparency at 157 nm. This important information serves as a starting point for 157 nm photoresist design.⁴²

Etch resistance, of course, must be incorporated into any 157 nm photoresist design. As in 193 nm lithography, simple aromatic groups are too absorbing to provide etch resistance in a 157 nm resist. The alicyclic groups used in ArF photoresists are currently seen as the best approach for providing etch resistance at 157 nm. The transparency of alicyclics might need to be improved by strategically placing electron-withdrawing groups on the rings. Gas-phase absorbance measurements on several fluorinated alicyclic model compounds are being carried out to determine the most effective locations of fluorine atoms to lower 157 nm absorbance.

For the photoresist to develop in aqueous base developer solutions, acidic functional groups must be incorporated into the matrix resin. In KrF photoresists phenolic groups are used to provide base solubility, but the aromatic ring absorbs strongly at 193 nm, so ArF resists use carboxylic acids. Unfortunately, typical phenols and carboxylic acids absorb too strongly at

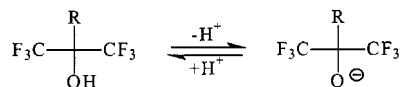


Figure 10. Structure of hexafluoro-2-propanol group with illustration of inductive stabilization

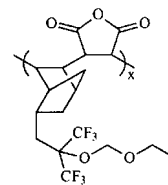


Figure 11. Prototype of a 157 nm photoresist used to validate the imaging capability of an acetal-protected hexafluoro-2-propanol group. This particular system would be strongly absorbing at 157 nm owing to the carbonyl groups in the MA unit, but successful imaging was carried out at 193 nm

157 nm to be used in photoresists for that wavelength. In fact, the MIT researchers concluded that any material containing π -systems is likely to be strongly absorbing at 157 nm. This means that acidic functional groups that rely on resonance stabilization may be unavailable for 157 nm photoresists and some other route must be used to provide acidic groups. Inductive stabilization does not require π -electrons and can give reasonably acidic groups. Inductively stabilized anions that lack π -electrons could possibly be utilized in 157 nm photoresists to provide base solubility. Hexafluoro-2-propanol (Fig. 10) is an example of a compound with a hydroxyl group that is fairly acidic due to inductive stabilization. The strongly electron-withdrawing trifluoromethyl groups give the compound an acid strength close to that of phenol.⁴³ Hexafluoro-2-propanol has in fact been previously used as an acidic functional group in photoresist designs for both KrF lithography⁴⁴ and ArF lithography.⁴⁵ Our research group has determined that hexafluoro-2-propanol is very transparent at 157 nm, making it an ideal choice for 157 nm photoresists.⁴⁶

For imaging to be possible at least some fraction of the acidic functional groups must be blocked with a labile protecting group. The most common protecting groups in current photoresists are *tert*-butyl carbonates and *tert*-butyl esters. These happen to be unsuited to 157 nm photoresists because they have highly absorbing carbonyl moieties. Acetal and ether protecting groups, on the other hand, have no carbonyl groups, which makes them potentially useful at 157 nm. A prototype resist using acetal-protected hexafluoro-2-propanol on a norbornene-maleic anhydride polymer (Fig. 11) was recently tested with 193 nm light and was shown to be a viable imaging combination.⁴⁷ The acetal-hexafluoro-2-propanol combination will likely be very important in 157 nm photoresist designs.

THIN-LAYER IMAGING FOR 157 nm LITHOGRAPHY

The challenge of finding of transparent materials for single-layer 157 nm photoresists has forced the industry to reconsider alternative imaging schemes. Thin-layer imaging has long been studied as an alternative to single-layer imaging. In fact, when research began on 193 nm lithographic systems, many felt that a thin-layer imaging technique would prevail as the dominant lithographic technology. In thin-layer imaging, photochemistry creates an etch mask only in the top layer (approximately 100 nm) of the resist. This etch mask is then used to transfer the image through a thicker resist layer by using an anisotropic dry etch process. Since only the top of the film need be exposed, materials that are relatively opaque at the exposure wavelength can be used. Thin-layer imaging systems also typically offer enhanced depth of focus and a relative insensitivity to underlying topography. The drawbacks of these systems are increased process complexity and manufacturing costs. These systems will therefore be used only when single-layer resist techniques are not possible.

There are a number of methods for implementing thin-layer imaging, but they can generally be grouped into two categories. (It is beyond the scope of this a paper to detail all work on bilayer and silylation resist chemistries. A comprehensive description of these subjects with references may be found in Ref. 4.) The first is a system in which two resist layers are coated one upon the other. The thin top layer generally contains silicon atoms and is imaged just like a traditional single-layer resist. After development of the top layer, the shallow relief image is transferred through a thicker resist layer using an anisotropic oxygen plasma etch. The silicon in the top layer oxidizes to form a highly etch-resistant material and consequently serves as an etch mask for the underlayer. In the region where the silicon-containing polymer dissolved away, no masking occurs and the underlayer material quickly etches away. The second type of system involves coating a single resist layer, then creating the etch mask in the top portion of this material. The incorporation of silicon into the resist is typically accomplished with a silylation process that incorporates silicon through the generation of covalent linkage to an active site in the polymer film. The availability of these active sites is controlled by exposure to radiation so that silylation occurs only in one region of the photoresist (either exposed or unexposed depending on the resist tone). The silylated regions then act as an etch mask for transferring the image.

Systems of this sort have rarely been used in manufacturing because of increased process complexity. The silylation systems also have an additional problem in that they almost universally yield features with a high degree of line edge roughness. The sources of line edge roughness have recently been elucidated⁴⁸⁻⁵⁰ and this knowledge has allowed these systems to be tailored to

print very high-resolution and very smooth features. At 157 nm, optical transparency is at a premium and any technology that reduces the transparency requirement is desirable. Thin-layer imaging techniques have re-emerged as leading alternatives to single-layer resists and may in fact become the technology of choice for 157 nm lithography.

LITHOGRAPHY AFTER OPTICAL LITHOGRAPHY

Many believe that photolithography with 157 nm light will be the last optical lithography technology to be developed. The industry is counting on one of the NGL (next generation lithography) alternatives such as extreme ultraviolet (EUV) or electron beam projection (SCALPEL) to emerge to replace optical lithography for sub-100 nm device production. The changeover to any of these processes will require the development of new high-resolution resist materials. As mentioned previously, the apparent resolution limit for the classical chemically amplified tBOC resist system was determined to be about 40 nm.¹⁵ Printing a 50 nm feature in this material would be a difficult task for any NGL if there is already 40 nm of intrinsic resist bias. Ways to improve resist resolution by limiting catalyst migration are under investigation, but to maintain chemical amplification the catalyst must maintain some amount of mobility, and any amount of catalyst mobility will lead to some loss of resolution. This trade-off requires more study.

In recent years, a radically different approach to patterning wafers has begun to emerge. Imprint lithography⁵¹ and micro-molding lithography^{52,53} are starting to show great promise. These techniques provide a way to skip the imaging and development steps of the traditional lithographic process and directly create resist relief images on the wafer substrate by simple molding and contact techniques. This offers significant potential cost advantages since they do not require imaging optics that are typically the most expensive piece of a lithographic tool. These processes also forego the need for expensive radiation sources needed by most NGL technologies. Sub-50 nm features have been printed with these techniques, and printable feature size appears to be limited only by the dimension of the feature that can be constructed in the mold/template. These techniques offer the potential to manufacture microdevices much more cost effectively than any of the currently contemplated photolithographic processes or NGL technologies. These 'simple' molding techniques may be the path to continued improvements in microelectronic devices.

REFERENCES

1. <http://www.amd.com>.
2. Willson CG, Dammel RA, Reiser A. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1997; **3051**: 28.

3. Dammel RA. *Diazonaphthoquinone-based Resists*. SPIE Optical Engineering Press: Bellingham, WA, 1993.
4. Thompson LF, Willson CG, Bowden MJ. *Introduction to Microlithography*. American Chemical Society: Washington, DC, 1994.
5. Reiser A. *Photoreactive Polymers—The Science and Technology of Resists*. John Wiley & Sons: New York, 1989.
6. Ehrlich DJ, Rothschild M. *Microelectron Eng.* 1989; **9**: 27.
7. Schenker RE, Eichner L, Vaidya H, Vaidya S, Oldham WG. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1995; **2440**: 118.
8. Fréchet JMJ, Ito H, Willson CG. *Proc. Microcircuit Eng.* 1982; 260.
9. Ito H, Willson CG. *Polym. Eng. Sci.* 1983; **23**: 1012.
10. Ito H, Willson CG. *ACS Symp Ser.* 1984; **242**: 11–23.
11. Ito H, Willson CG, Fréchet JMJ. US Patent 4 491 628, 1985.
12. Crivello JV, Lam JH. *J. Polym. Sci.: Polym Chem. Ed.* 1979; **17**: 977.
13. Crivello JV. *J. Polym. Sci. A.* 1999; **37**: 4241.
14. MacDonald SA, Willson CG, Fréchet JMJ. *Acc. Chem. Res.* 1994; **27**: 150.
15. Umbach CP, Broers AN, Willson CG, Koch R, Laibowitz RB. *J. Vac. Sci. Technol. B* 1988; **6**: 319.
16. Umbach CP, Broers AN, Willson CG, Koch R, Laibowitz RB. *IBM J. Res. Dev.* 1988; **32**: 454.
17. Zuniga M, Wallraff G, Tomacruz E, Smith B, Larson C, Hinsberg WD, Neureuther AR. *J. Vac. Sci. Technol. B* 1993; **11**: 2862.
18. Postnikov SV, Stewart MD, Tran HV, Nierode MA, Medeiros DR, Cao T, Byers J, Webber SE, Willson CG. *J. Vac. Sci. Technol. B* 1999; **17**: 3335.
19. Wallraff GM, Hinsberg WD, Houle FA, Morrison M, Larson CE, Sanchez M, Hoffnagle J, Brock PJ, Breyta G. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1999; **3678**: 138.
20. Croffie E, Cheng M, Neureuther A. *J. Vac. Sci. Technol. B* 1999; **17**: 3339.
21. Fedenyshyn TH, Thackeray JW, Georger JH, Denison MD. *J. Vac. Sci. Technol. B* 1994; **12**: 3888.
22. Nalamasu O, Reichmanis E, Hanson JE, Kanga RS, Heimbrook LA, Enerson AB, Baiocchi FA, Vaidya S. *Polym. Eng. Sci.* 1992; **32**: 1565.
23. MacDonald SA, Hinsberg WD, Wendt HR, Clecak NJ, Willson CG, Snyder CD. *Chem. Mater.* 1993; **5**: 348.
24. Ito H, Breyta G, Hofer D, Sooriyakunaran R, Petrillo K, Seeger D. *J. Photopolym. Sci. Technol.* 1994; **7**: 433.
25. Breyta G, Hofer DC, Ito H, Seeger D, Petrillo K, Moritz H, Fischer T. *J. Photopolym. Sci. Technol.* 1994; **7**: 449.
26. Goken H, Esho S, Ohnishi Y. *J. Electrochem. Soc.* 1983; **130**: 143.
27. Allen RD, Wallraff GM, Hinsberg WD, Conley WE, Kunz RR. *J. Photopolym. Sci. Technol.* 1993; **6**: 575.
28. Kunz RR, Allen RD, Hinsberg WD, Wallraff GM. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1993; **1925**: 167.
29. Kaimoto Y, Nozaki K, Takechi S, Abe N. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1992; **1672**: 66.
30. Allen RD, Wallraff GM, Hofer DC, Kunz RR. *IBM J. Res. Dev.* 1997; **41**: 95.
31. Nozaki K, Watanabe K, Yano E, Kotachi A, Takechi S, Hanyu E. *J. Photopolym. Sci. Technol.* 1996; **9**: 509.
32. Iwasa S, Maeda K, Nakano K, Ohfuji T, Hasegawa E. *J. Photopolym. Sci. Technol.* 1996; **9**: 447.
33. Shida N, Ushirogouchi T, Asakawa K, Nakase M. *J. Photopolym. Sci. Technol.* 1996; **9**: 457.
34. Okoroanyanwu U, Shimokawa T, Medeiros D, Willson CG, Fréchet JMJ, Niu JQ, Byers J, Allen RD. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1997; **3049**: 92.
35. Okoroanyanwu U, Shimokawa T, Byers J, Willson CG. *Chem. Mater.* 1998; **10**: 3319.
36. Patterson K, Okoroanyanwu U, Shimokawa T, Cho S, Byers J, Willson CG. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1998; **3333**: 425.
37. Houlihan FM, Wallow TI, Nalamasu O, Reichmanis E. *Macromolecules* 1997; **30**: 6517.
38. Byers J, Patterson K, Cho S, McCallum M, Willson CG. *J. Photopolym. Sci. Technol.* 1998; **11**: 465.
39. Yamachika M, Patterson K, Cho S, Rager T, Yamada S, Byers J, Paniez PJ, Mortini B, Gally S, Sassoulas P-O, Willson CG. *J. Photopolym. Sci. Technol.* 1999; **12**: 553.
40. Semiconductor Industry Association Roadmap, 1999, http://public.itrs.net/files/1999_SIA_Roadmap/Home.htm.
41. Palik ED, (ed). *Handbook of Optical Constants of Solids*. Academic Press: San Diego, 1991.
42. Kunz RR, Bloomstein TM, Hardy DE, Goodman RB, Downs DK, Curtin JE. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1999; **3768**: 13.
43. Grandler JR, Jencks WP. *J. Am. Chem. Soc.* 1982; **104**: 1937.
44. Przybilla KJ, Roschert H, Pawlowski G. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1992; **1672**: 500.
45. Ito H, Seehof N, Nakayama T, Ueda M. *ACS Symp. Ser.* 1998; **706**: Chapt. 16.
46. Patterson K, Somervell MH, Willson CG. *Solid State Technol.* 2000; **3**: 43.
47. Patterson K, Yamachika M, Hung R, Brodsky C, Yamada S, Somervell M, Osborn B, Hall D, Dukovic G, Byers J, Conley W, Willson CG. *Proc. Soc. Photo-Opt. Instrum. Eng.* 2000; **3999**: in press.
48. Vertommen J, Klippert W, Goethals AM, Van Roey F. *J. Photopolym. Sci. Technol.* 1998; **11**: 597.
49. Kim HG, Kim MS, Bok CK, Park BJ, Kim JW, Baik KH, Lee DH. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1998; **3333**: 493.
50. Somervell MH, Fryer DS, Osborn B, Cho S, Patterson K, Byers JD, Willson CG. *Proc. Soc. Photo-Opt. Instrum. Eng.* 2000; **3999**: in press.
51. Chou SY, Krauss P, Zhang W, Guo L, Zhuang L. *J. Vac. Sci. Technol. B* 1996; **15**: 2897.
52. Ruchhoeft P, Colburn M, Choi B, Nounu H, Johnson S, Bailey T, Damle S, Stewart M, Ekerdt J, Sreenivasan SV, Wolfe JC, Willson CG. *J. Vac. Sci. Technol. B* 1999; **17**: 2965.
53. Colburn M, Johnson S, Stewart M, Damle S, Jin B, Bailey T, Wedlake M, Michaelson T, Sreenivasan SV, Ekerdt J, Willson CG. *Proc. Soc. Photo-Opt. Instrum. Eng.* 1999; **3676**: 379.