

Negative photoresists for optical lithography

by J. M. Shaw
J. D. Gelorme
N. C. LaBianca
W. E. Conley
S. J. Holmes

Negative photoresists are materials that become insoluble in developing solutions when exposed to optical radiation. They were the first systems used to pattern semiconductor devices, and still comprise the largest segment of the photoresist industry because they are widely used to define the circuitry in printed wiring boards. However, the current use of negative resists in the semiconductor industry has been limited by past difficulties in achieving high-resolution patterns. Recent advances in the chemistry of negative-resist systems, however, have provided materials with wide processing latitude and high resolution that are used to manufacture IBM's advanced CMOS devices and to achieve high-aspect-ratio patterns for micromachining applications. This paper provides an overview of the history and chemistry of negative-resist systems and their development in IBM.

1. Introduction

The majority of polymers, when exposed to ultraviolet light in the range from 200 to 300 nm (~4 eV to 6 eV), form "radical species" which can result in cross-linking, increased molecular weight, insolubilization, and film embrittlement. While industries such as the automotive and aerospace have concentrated research activities on

inhibiting these reactions to extend the life of plastic coatings and components, the semiconductor industry has used this effect to its advantage to produce polymeric stencils resistant to the acids and bases used to fabricate semiconductor devices and circuitry. As shown in **Figure 1**, these photosensitive films, which become insoluble in solvents or water-based developers upon exposure to radiation, form "negative" patterns which are used as temporary stencils to delineate many levels of circuitry in semiconductor devices and printed wiring boards (PWBs). This insolubilization can be achieved by using materials which upon UV exposure either 1) increase in molecular weight, or 2) are photochemically rearranged to form new insoluble products. To increase molecular weight, photoinitiators are generally used that can generate free radicals or strong acids to facilitate polymeric cross-linking or the photopolymerization of monomeric or oligomeric species. Without an increase in molecular weight, negative patterns can be achieved by the photochemical formation of hydrophobic or hydrophilic groups which provide preferential solubility between the exposed and unexposed resist film.

Over the past thirty years, chemists and engineers have been able to provide a wide variety of resists, both negative (insolubilize upon exposure to radiation) and positive (solubilize upon exposure to radiation) to answer the needs of a growing industry. As seen in **Figure 2**, negative resists currently comprise the largest segment of the photoresist market. The choice of whether to use a

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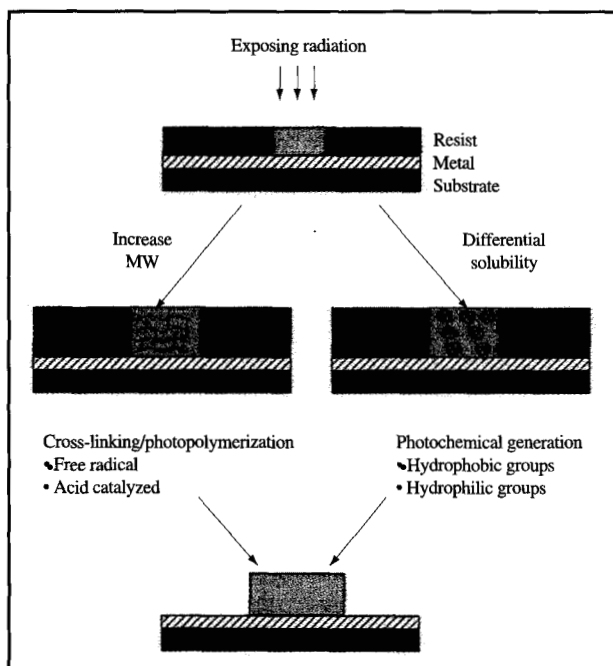


Figure 1

Schematic of the patterning of negative resist systems.

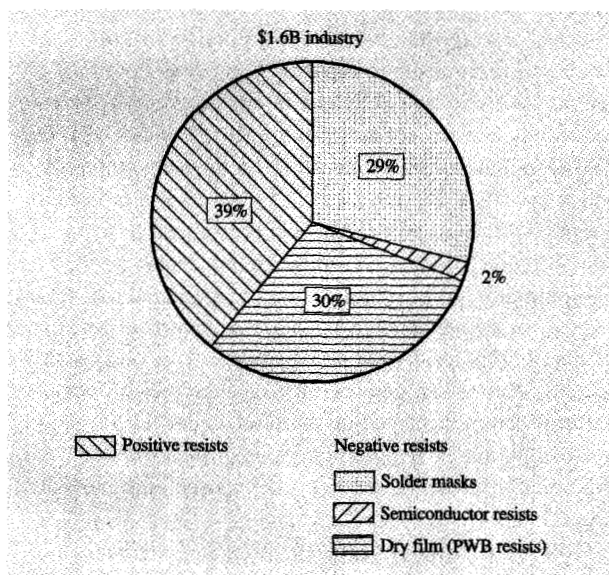


Figure 2

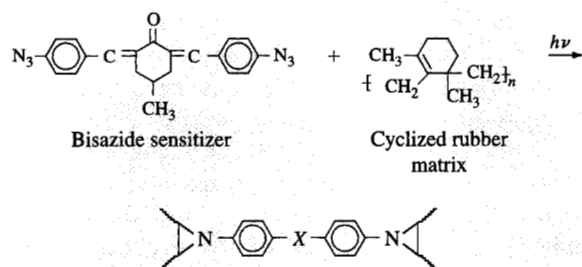
Worldwide photoresist market (1995) for semiconductor and printed wiring boards (Source: Prismark and Rose Associates).

of processing, and cost. Negative resists continue to dominate the fabrication of printed wiring boards, where manufacturing throughput and cost are paramount issues. Positive resists are largely used for the patterning of high-resolution semiconductor devices, although advances in the resolution capability of some negative systems, and the advantage of patterning them on certain device levels, have generated increased interest and usage. A negative resist, because of its wider processing latitude and high resolution, is currently used to pattern critical levels of IBM's advanced CMOS logic devices, where the control of linewidth and its variation across the chip is key to performance. This paper provides an overview of negative resists, including a description of recent work on advanced systems for the fabrication of semiconductors, and the micromachining of microelectromechanical devices (MEMs).

2. Negative photoresists for semiconductors and PWBs

• Free-radical-initiated resist systems

The first negative resists designed specifically to address the growing needs of the semiconductor industry were introduced in the 1960s and were based upon *free-radical-initiated photocross-linking* or *photopolymerization* processes. The newly developed lithography tools for the semiconductor industry used the output of mercury arc lamps in the "near UV" at wavelengths from 365 nm to 436 nm; they required a photosensitive system that would be able to form pinhole-free thin films that were resistant to the acids and bases used to pattern devices, with adhesion to unique semiconductor surfaces and metals. Kodak introduced a system called KTRF consisting of a bis-aryldiazide photosensitive cross-linking agent which absorbed in the near UV, with a polyisoprene cyclized polymer to provide the necessary film-forming and adhesion properties [1]. As seen in **Formula I**, upon exposure the resist cross-links through a free-radical mechanism where nitrene is inserted into the polymeric backbone [2], and the unexposed film is removed using aromatic solvents as developing solutions. However, this resist has several disadvantages: 1) The presence of oxygen acts as a free-radical scavenger, inhibiting cross-linking, and the resist must be exposed under vacuum or nitrogen; 2) the solvent developer swells the cross-linked negative image, causing degradation of the pattern and limiting resolution to 2 μm in a 1- μm -thick coating; and 3) the aromatic solvent developer may pose environmental, health, and safety concerns. This system met semiconductor manufacturing requirements until the mid-1970s, when the demand for increased circuit density generated a need to provide a better photoresist, although similar systems are still used for less demanding applications.



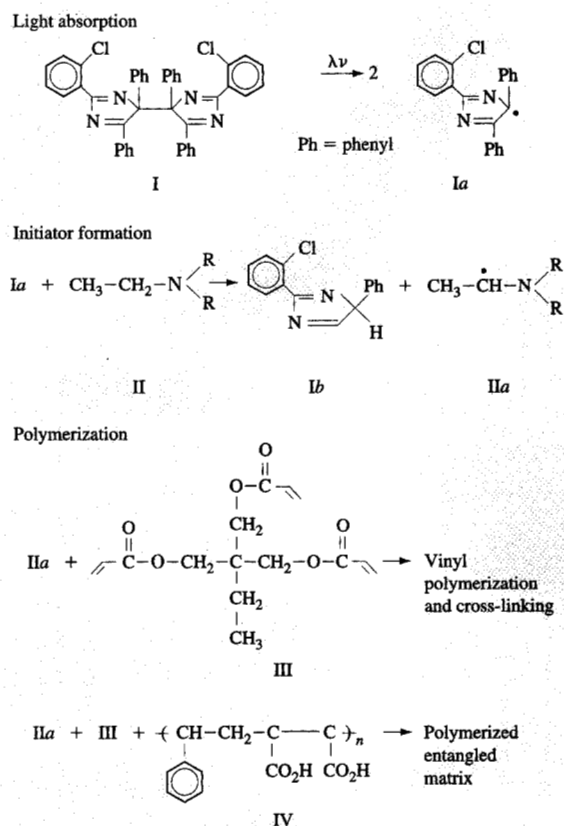
Formula I

KTFR (free-radical-initiated photocross-linking). X = aliphatic or aromatic group.

However, for the fabrication of printed wiring boards where resolution requirements are less severe, *free-radical photopolymerization* provides low-cost, highly sensitive systems that are the mainstay of the industry. Dry-film photoresists, introduced by DuPont in 1968 [3], are the most widely used. They consist of a photopolymerizable layer that is sandwiched between a polyester support film and a separator sheet. This dry film has a number of advantages. After removal of the separator sheet, the dry film is laminated to the substrate and (unlike liquid resists) can bridge or "tent" over the plated-through holes in PWBs. Also, the polyester cover sheet protects the resist film from oxygen diffusion, which would inhibit the cross-linking reaction. Throughout the 1970s these resist systems were developed in chlorinated solvents, but aqueous-base-developable systems are now available [4, 5]. A typical dry-film resist system is shown in **Formula II** and described in detail in Reference [5]. It comprises 1) an initiator which absorbs radiation, forming an imidazole radical (Ia) which abstracts hydrogen from a tertiary amine to form a radical (IIa) which initiates the polymerization process; 2) polyfunctional photopolymerizable monomers (III), which react to form a highly cross-linked, chemically resistant structure; and 3) a binder to provide toughness and film-forming properties, typically a styrene/maleic acid polymer (IV). To meet the ever-increasing wiring density demands, the resolution capability of these materials has steadily improved from 200- μm circuit line dimensions in the 1970s to a current capability of <75 μm .

• Positive-resist modifications

Negative semiconductor resists such as KTFR, as described above, did not meet the resolution requirements for the semiconductor industry in the early 1970s because of swelling of the developed pattern. A new "positive" material was developed based on diazo chemistry that had



Formula II

Typical dry-film resist (free-radical photopolymerization).

been patented by Azoplate [6]. As opposed to KTFR, where the differentiation in the developing solvent between the exposed and unexposed regions relies upon a molecular weight increase in the system through cross-linking, diazo-type resists depend upon a dramatic change in polarity to achieve differential solubility. The basic resist is a two-component system where a low-molecular-weight phenolic-based resin is mixed with a diazoketone derivative. The phenolic resin provides excellent film-forming properties and is highly soluble in basic solutions. The addition of a diazonaphthoquinone photosensitizer acts as a dissolution inhibitor, and dramatically reduces the solubility of the unexposed film in basic solutions. However, upon exposure, the diazo derivative undergoes molecular rearrangement to form a carboxylic acid, and the exposed area becomes soluble in basic developers, forming a positive image. A detailed review of the chemistry of this system has been provided by a number of authors [7-9].

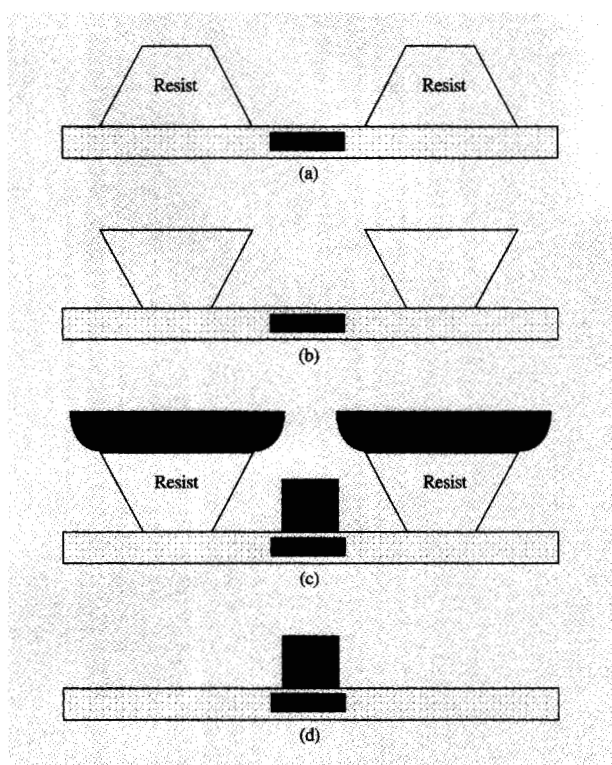


Figure 3

Resist profile requirements for lift-off metallization: (a) Typical positive resist profile; (b) undercut resist profile; (c) and (d) lift-off metallization process.

This positive system had a number of advantages for the growing semiconductor industry. Resolution was enhanced, since the resist was not cross-linked and did not swell in water-based developing solutions. A variety of diazoketone photoactive compounds could be engineered to optimize their absorption characteristics in the "near-UV" and "mid-UV (3130 Å)," providing extendibility to future-generation optical tools [10]. The aqueous-based developing solutions were safer and easier to use in manufacturing, and it was also found that the yield of many lithography levels, such as the device contact level, could be increased by using "dark-field" masks in conjunction with positive resists. For these reasons, positive diazo-type resists have been the backbone of the industry, and innovative chemistry was able to extend their use for a number of manufacturing applications that might otherwise have required the development of new negative resists.

For example, to fabricate high-density metal wiring for device interconnection on bipolar chips, it was necessary to convert a typical diazo resist profile [Figure 3(a)] to an

"undercut" resist profile [Figure 3(b)] in order to provide a stencil for evaporated metal where the excess was removed by a "lift-off" process [Figures 3(c) and 3(d)]. This is very difficult to achieve in positive resists, because the optical exposure dose (and hence the development rate of the system) is greater at the surface than at the resist/substrate interface, resulting in the profile seen in Figure 3(a). Conversely, a negative resist which forms more insoluble products at the resist surface than at the resist/substrate interface easily provides an "undercut" profile. However, rather than developing and implementing new negative resists in manufacturing, it was found possible to provide this profile by modifying typical diazo photoresists using a number of techniques. The first method, shown in Figure 4(a), treated the surface of a resist film with an aromatic solvent to provide a surface layer which developed at a much slower rate than the bulk resist film, providing an undercut profile during development in basic solutions [11]. Because of increasing environmental and safety concerns, this technology was replaced in manufacturing by an "image-reversal" process [Figure 4(b)]. By adding a basic molecule such as imidazole to the diazo resist formulation, it was found possible to transform a positive image that was easily removed in developer to a *negative* pattern that was resistant to basic solutions and had an undercut profile owing to the optical absorption of the system. The imidazole would react with the carboxylic acids generated upon exposure. After the film had been baked and blanket-exposed, the exposed image was less soluble in basic developers than the unexposed resist, forming a negative image which was used as a stencil in manufacturing to evaporate high-aspect-ratio metal [12–14]. However, the next-generation chips required even greater density, higher-aspect-ratio metal, and linewidth control, and it was found necessary to use reactive ion etching to form the "lift-off" pattern [15]. As shown schematically in Figure 4(c), rather than developing new resists containing silicon that would provide a photoimageable oxygen plasma etch barrier, chemists were able to modify the developed resist pattern by using a process called *silylation*. In this process, reactive monomers containing silicon functionalities are diffused into the patterned diazo-resist stencil, using an inert solvent as a carrier. These monomers react with the novolac base polymer to provide the necessary plasma etch resistance [16–18]. A silylation process is still in use today to pattern high-aspect-ratio metallurgy [19, 20].

Continued development, optimization, and innovation in the materials and processing of these diazo resist systems have answered the semiconductor requirements, from the 2- μm lithography of the 1970s to current 16Mb devices with 0.5- μm ground rules. However, it was realized that continued scaling of device geometry would require new

optical lithography tools utilizing the shorter wavelengths in the deep-UV (DUV) region of the spectrum (~250 nm). In the early 1980s, research projects were initiated to develop the optical tooling and resist systems necessary for future chip generations. The first DUV projection tool, PE-500, was provided by Perkin-Elmer [21]. Because laser sources at that time were not reliable, it utilized a high-pressure mercury arc as a light source, and the output intensity was severely reduced through self-quenching of the mercury vapor. Typical diazo-type resist systems were not sensitive enough to achieve adequate manufacturing throughput, and too absorbing to achieve high resolution. Totally new resist systems had to be designed to pattern future-generation chips.

- *Chemically amplified negative resists*

One of the most promising approaches to addressing future lithographic needs utilized discoveries in the late 1970s that photolysis of certain thermally stable onium salts [22] produced strong acids that could be used to design new photoimaging systems [23, 24]. These strong acids could function as catalysts to initiate many chemical reactions, providing a path to highly sensitive resists and coatings. Compared to the conventional free-radical initiators, the onium salts have excellent thermal stability, are not sensitive to oxygen, and exhibit no "dark" or side reactions in solution. This led to the development of novel negative-resist systems in which differential solubility between the exposed and unexposed areas of the resist film was achieved by using the photogenerated acid as a catalyst to either increase the molecular weight of the system or generate chemical changes in polarity that would provide different solubility. The increase in molecular weight could be achieved by *cationically polymerizing* monomers such as epoxies and vinyl compounds, or by enabling *condensation* reactions between phenol formaldehyde resins and amino-based cross-linkers. Changes in polarity could be achieved through the *acid-catalyzed deprotection* of a variety of esters. In addition, during this process the by-product of the deprotection regenerates the acid, hence the term *chemical amplification*. Negative resists based on all of these mechanisms have been developed; they are described in the following sections.

In 1982 Ito and Willson [25] reported the first "chemically amplified" resist for DUV applications based on an *acid-catalyzed deprotection* mechanism. Here, the catalytic species generated by the irradiated onium salt created many chemical changes that provided differential solubility between exposed and unexposed areas. This resulted in a change in polarity rather than an increase in molecular weight. This "gain" mechanism provided much higher quantum efficiency than typical diazo-type reactions. The first DUV negative resist system used

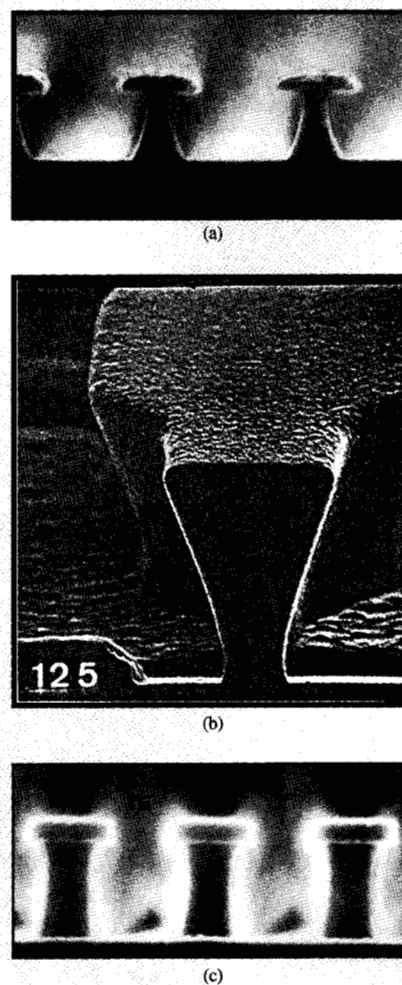
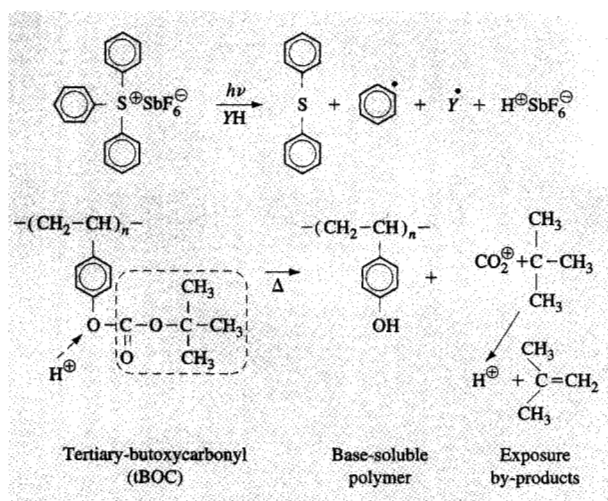


Figure 4

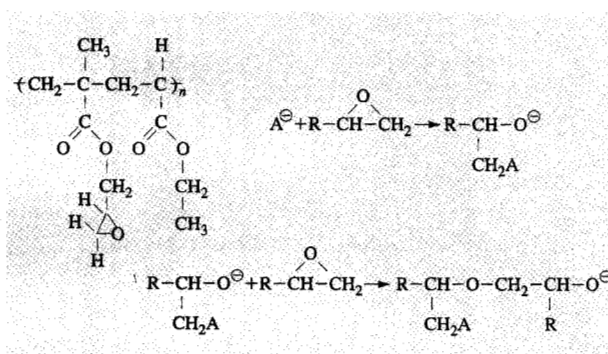
Techniques for modifying diazo photoresists: (a) Chlorobenzene soak; (b) image reversal process (SEM courtesy C. Hamel, IBM internal report); (c) silylation process.

in semiconductor manufacturing was based upon poly(4-t-butoxycarbonyloxystyrene), tBOC, and a triphenylsulfonium hexafluoroantimonate onium salt. Upon exposure in the deep UV, and subsequent baking to diffuse the photogenerated acid and complete the reaction, the acid cleaved the labile tBOC protecting groups to form a polar polyvinyl phenolic polymer, as seen in **Formula III**. The unexposed resist was removed by using a nonpolar solvent, forming a negative image. This system, known as tBOC resist, provided the exposure sensitivity required for product throughput on the DUV Perkin-Elmer tools and was used to manufacture 1Mb DRAMs in the late 1980s [26]. However, it was found



Formula III

tBOC resist (acid-catalyzed deprotection). YH = monomer or solvent.

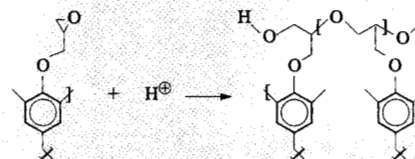


Formula IV

Aliphatic epoxy (anionic cross-linking).

difficult to control the linewidth of this new chemically amplified system in a manufacturing environment. The sensitivity of the photoresist was affected by airborne chemical contaminants. Special carbon filters had to be installed, and coatings had to be used to protect resist film from diffusion of contaminants. Also, the diffusion of the acid and hence the sensitivity and resolution of the system were found to depend upon precise control of prebake temperature, time between exposure and post-exposure bake (PEB), and the time and temperature of the PEB process itself.

Concurrently, other resists were investigated to try to enhance the process latitude and reduce the

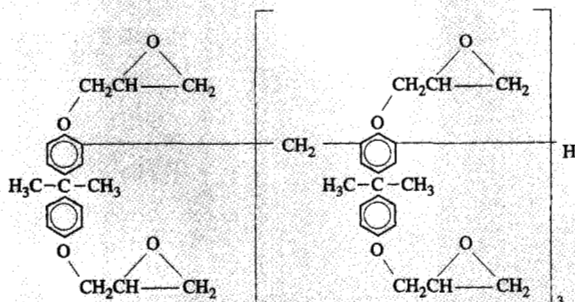


Formula V

Aromatic epoxy (acid-catalyzed cationic cross-linking).

manufacturing cost of UV resists. Epoxy materials were attractive alternatives, since there are a large variety of epoxidized polymers available in both solid and liquid form. These materials generally offer excellent adhesion to semiconductor surfaces, good sensitivity, and low cost. An epoxy derivative can be chosen to provide 1) optimum sensitivity, which is a function of the number of epoxy groups per molecule; 2) plasma resistance and thermal stability, which are functions of the backbone chemistry; and 3) resolution and contrast, which are functions of the molecular weight and dispersivity. In 1974, Bell Laboratories had developed an electron-beam resist based on a high-molecular-weight epoxy resin, a glycidyl acrylate-ethyl acrylate copolymer shown in **Formula IV** [27]. When exposed to high-energy e-beam radiation, the material generates a reactive ionic species that subsequently reacts with an epoxy functionality to form a cross-linked system. Although it was the first resist used to fabricate optical masks, the resist properties were not adequate for fabrication of high-resolution semiconductor devices. The developer induced swelling in the pattern because of the high molecular weight of the resin. The optical sensitivity in the DUV was poor, and because the resist was based on an aliphatic backbone and contained no aromatic functionalities, the thermal stability and plasma resistance of the system were not adequate.

Because of the need for high-performance negative resists in the DUV, one of the first systems investigated was based on the *cationic ring-opening polymerization* of epoxy resins. Initial work on UV-curable coatings [23, 24] and resist systems [28-30] demonstrated their potential. While solvent-induced swelling had degraded the resolution capability of the high-molecular-weight e-beam resists, it was hoped that this could be avoided by choosing low-molecular-weight, multifunctionalized epoxy derivatives that would form cross-linked, high- T_g films. This concurrent increase in cross-link density could not only reduce solvent swelling, but also limit the diffusion of photogenerated acid during the postexposure bake

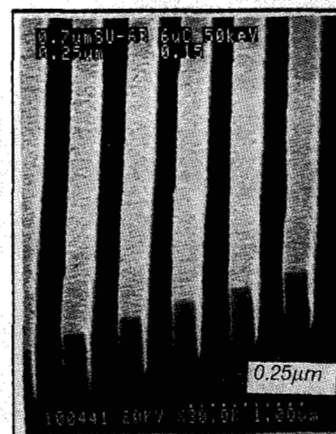


Formula VI

Glycidyl ether of bisphenol A—SU-8.

process, which can lead to linewidth degradation. Also, the substitution of epoxy functionalities on an aromatic backbone should provide thermal stability and plasma etch resistance. The first material evaluated was an orthocresol novolac glycidyl ether resin used as a chip encapsulant and commercially available from Dow as Quatrex[®] electronic-grade materials. This multifunctional material, shown in **Formula V**, had a low molecular weight of ~4000. When formulated with a photoacid generator, this simple, low-cost epoxy photoresist (EPR) demonstrated that solvent-developable resist formulations could fabricate submicron resist patterns using the DUV PE-500 exposure tool, and reduce the dependence on bake time and temperature [31].

Both the chemically amplified negative resist system, tBOC, and the acid-catalyzed EPR would have been capable of patterning the 1- μm ground rules required for the 1Mb chip. However, the difficulty in implementing new tooling, controlling bake processes, fabricating 1 $\times$ mask technology, and developing new resist systems had impacts on cost and scheduling. Advances in diazo resist systems, and tool improvements such as scaling the exposure wavelength and the numerical aperture (NA) of near-UV tools, provided a more cost-effective way to fabricate semiconductor chips with gate structures down to 0.5 μm in resolution. While DUV resists would not be needed for a few more chip generations, the early experience served as an important learning vehicle. The effort to optimize these systems over the next five years led to development of the resists currently used to manufacture all CMOS logic at 0.35- μm ground rules. The APEX positive resist system is described in a companion paper [32]. The following section describes the path to obtaining a high-resolution negative resist, CGR, used to fabricate the critical structures.



(a)



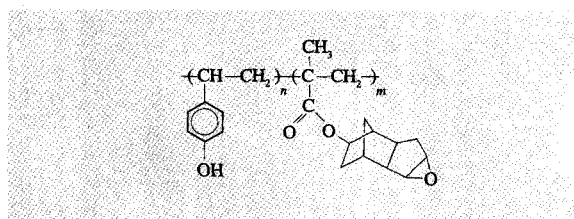
(b)

Figure 5

SU-8 images patterned using 50-keV electron-beam exposure (0.25- μm lines, 0.15- μm spaces, aspect ratio 4:1).

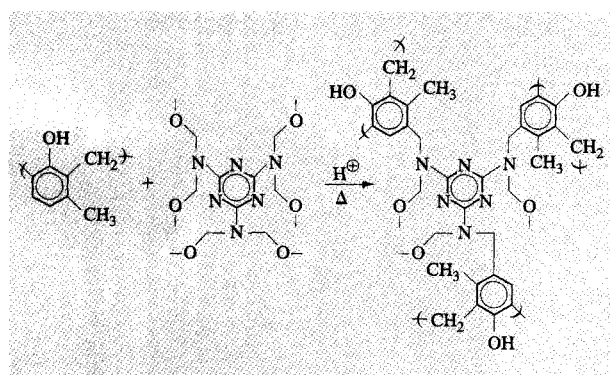
• High-resolution negative resists

Because of the promise shown in the first-generation epoxy DUV resist, work to improve these systems continued, and it was decided to investigate materials with high levels of epoxy functionalities in order to increase cross-linking density. **Formula VI** depicts a multifunctional glycidyl ether derivative of bisphenol-A novolac, available from Shell Chemical and known as EPON[®] resin SU-8, which provides the highest epoxy functionality commercially available. Upon exposure to either UV [33], e-beam, or X-ray radiation, it forms a ladderlike structure with a high cross-linking density and a T_g of more than 200°C. As seen in **Figure 5**, its versatile imaging capability has been used to fabricate advanced 0.25- μm and 0.1- μm devices using e-beam lithography [34]. The low molecular



Formula VII

Cycloaliphatic epoxy/hydroxystyrene copolymer.

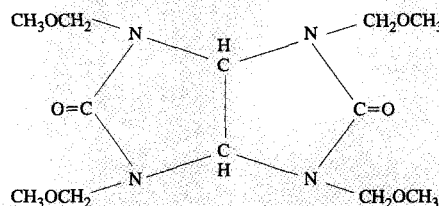


Formula VIII

Acid-catalyzed condensation reaction of aminoplast cross-linker with a novolac resin.

weight of the resin provides high contrast and excellent solubility and planarizing capability, and the high epoxy functionality provides sensitivity. Although the pattern is developed using a solvent, it is one of the highest-resolution systems yet developed, and it demonstrates the capability of cross-linked negative resists. It is described in greater detail in the section on micromachining.

The first-generation cross-linked negative resists were developed using organic solvents, and it was necessary to provide new systems that could be developed in aqueous basic solutions to be compatible with diazo systems already in use, and to meet safety requirements in a manufacturing environment. An initial effort was made to blend or copolymerize cycloaliphatic epoxies with base-soluble novolacs (**Formula VII**). While they were base-soluble, problems due to shelf stability, difficult synthetic procedures, and residue formation made these systems difficult to implement in manufacturing. A different approach was reported by Feeley [35] at Rohm and Haas in 1986. Shown in **Formula VIII**, it consists of an *acid-catalyzed condensation reaction* between an aminoplast



Formula IX

Powderlink 1174 cross-linker.

cross-linker such as a urea and melamine formaldehyde with a base-developable resin such as a novolac or poly(hydroxystyrene). These early resists had low shelf stability because the amino cross-linking agents were not stable; they were prone to self-reaction because of impurities from their industrial-scale manufacturing that were very difficult to eliminate. Also, the image stability and resolution were not adequate for the 0.35- μm lithography required for the 64Mb devices.

Several key improvements to this basic chemistry resulted in a negative resist called CGR, which is currently used to manufacture all critical levels of advanced CMOS logic devices [36, 37]. First, it was important to control the diffusion of photogenerated acid during the post-exposure bake process. The literature indicates that diffusion of photocatalyzing acid species is critical to both resolution and dimensional control characteristics of positive, and presumably negative, resists that rely on this chemistry. In positive chemically amplified systems, the time between exposure and bake as well as the time and temperature of the PEB process must be very tightly controlled in order to ensure reproducible linewidth dimensions. However, it had previously been seen in the epoxy photoresist (EPR) that negative resists, which increase in T_g (cross-link) upon baking after exposure, provided a wider processing window with less dependence on PEB time and temperature. During the post-exposure bake of the CGR resist, the photogenerated acid cross-links the resist, which concurrently increases the T_g and decreases the polar functionalities of the system. Therefore, it was important to understand and optimize the parameters controlling acid diffusion in order to further improve the performance of the negative resist chemistry shown in **Formula VIII**. Diffusion of any species through a polymer matrix at various temperatures can be directly related to the viscosity or to other measurements of flow phenomena, such as the modulus, of that polymer. This study of flow phenomena, known as *rheological analysis*, was used for

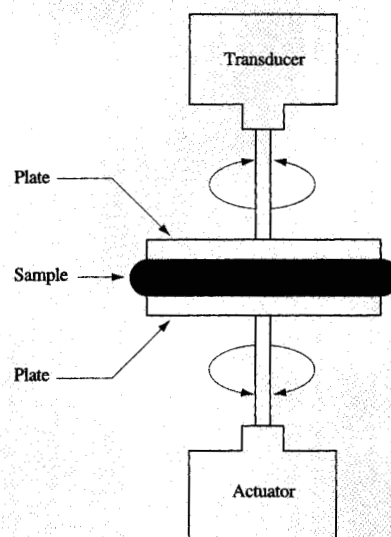
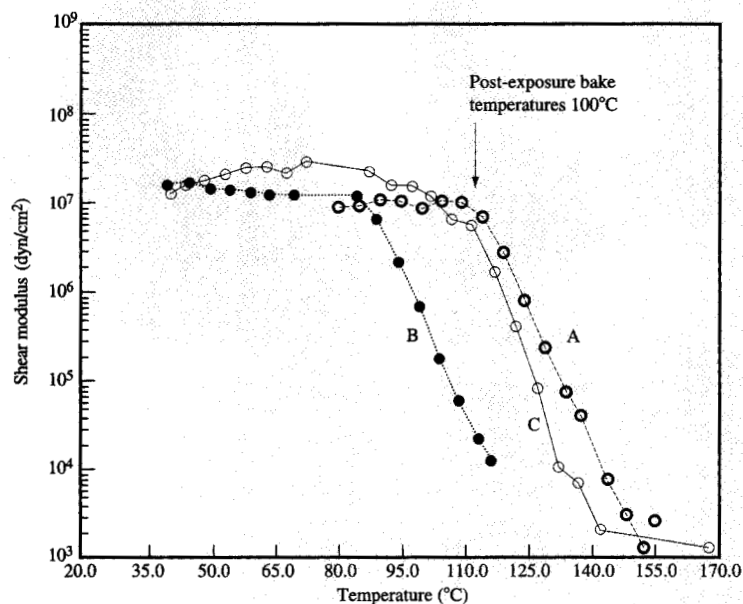


Figure 6

(a) Rheological characterization of negative resists. Plots are of the shear modulus of resists containing no cross-linker, Curve A ($T_g = 113^\circ\text{C}$); 20% liquid cross-linker, Curve B ($T_g = 80^\circ\text{C}$); and 5% solid cross-linker, Curve C ($T_g = 107^\circ\text{C}$). (b) Schematic of instrumentation for rheological measurement.

the first time to gain an understanding of acid diffusion. Rheological analysis which measures shear modulus vs. temperature, as shown in **Figure 6**, revealed that the commonly used liquid aminoplast cross-linking agents present in commercially available resists were plasticizing or softening the resist film during baking, and tended to lower the T_g of the material. The T_g of unexposed Shipley Negative Resist (SNR® 248)* is much lower than the recommended PEB of 100°C which was necessary to complete the cross-linking reaction after exposure. A new amino modifier (**Formula IX**) was identified that had a number of advantages. This new cross-linker, Powderlink® 1174 (a product of Cytek Industries, Inc.), was a solid at room temperature, with a high melting point of $90\text{--}110^\circ\text{C}$. When this modifier was incorporated in the formulation, the viscosity of the CGR at common PEB temperatures was 100 times greater than other negative systems, and, as seen in **Figure 6**, the T_g of the unexposed resist is equal to or very close to the PEB temperature. It is clear, then, that it is possible to achieve the minimum feature resolution by completing the post-exposure bake at a temperature that would provide the minimum flow or

distortion (i.e., at or slightly above the T_g of the resist). Because of these improvements, the resist is less sensitive to PEB temperature conditions, so that the controls on the bake temperature are not as stringent. In addition to imparting enhanced stability during processing, the modifier eliminated the problem of resist instability during storage. Since the modifier could be purified by recrystallization, formaldehyde and acidic contaminants were easily removed, and the shelf stability problem of the photoresist solutions was eliminated.

This negative-resist chemistry has a number of advantages. The resist does not require a topcoat to protect it from chemical vapors, since 1) it is less sensitive to basic contaminants because aminoplast resins already contain a tertiary amine functionality; and 2) very few reactive sites are required to turn the exposed area into an infinite cross-linked network, which dramatically increases differential solubility. Before the post-exposure bake, the resist has a T_g similar to the recommended PEB temperature of 100°C , which serves to control the initial diffusion and distortion. During the PEB cycle, diffusion can be further reduced, as the resist increases in T_g and the polar functionalities which may serve as diffusion

*Now replaced by SNR 200.

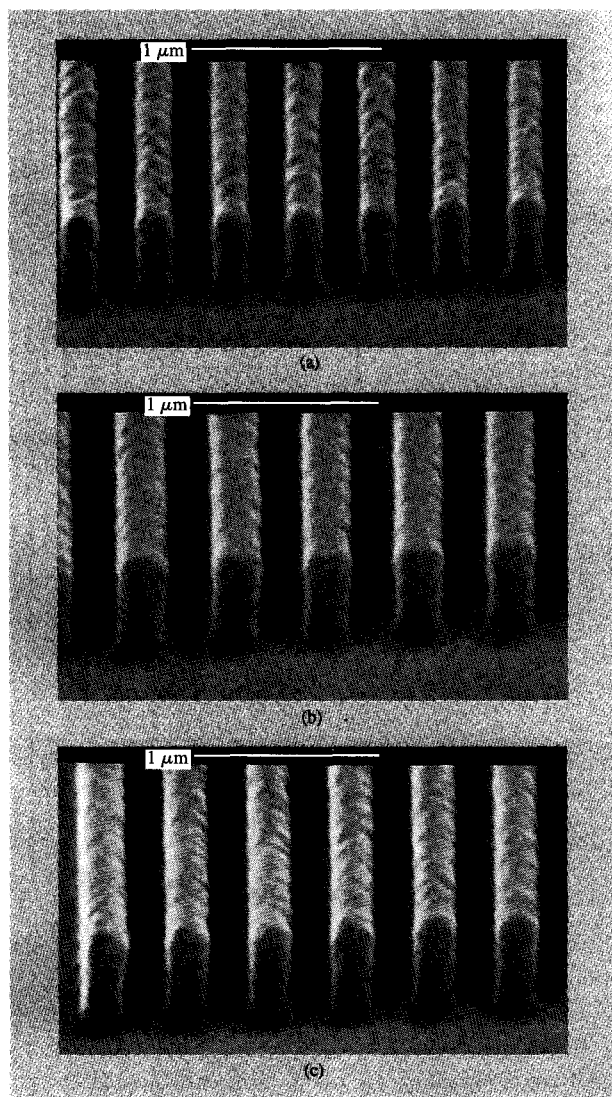


Figure 7

CGR resolution exposed on a Micrascan II optical exposure tool at 248 nm ($NA = 0.5$): (a) 200 nm; (b) 225 nm; (c) 250 nm.

paths [38] are decreasing. Also, because the exposed image is cross-linked, there is less dependence on developer time and temperature conditions, and the exposed image can be overdeveloped without affecting linewidth dimensions.

The combination of the enhanced processing properties of CGR, its excellent resolution capability, and the ability to use a dark-field mask to reduce reflections in the lens and resist [39, 40] has led to tighter control of the linewidth across the chip. As shown in Reference [41, Figure 13], this tight control of the channel length is critical to achieving device performance and yield [41–43].

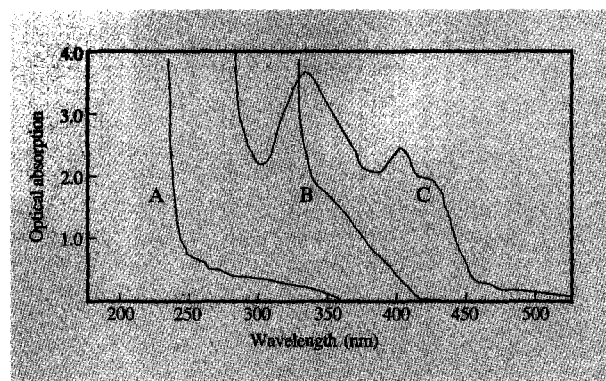


Figure 8

Optical absorption of resists used for micromachining: Curve A, 25 μm of SU-8; Curve B, 25 μm of dry-film RISTON® T-168 resist; Curve C, 10 μm of positive diazo resist.

Reference [41, Figure 15(a)] compares the linewidth control that can be achieved with APEX, a positive resist, where isolated lines are 8% larger than nested lines, and that of a negative CGR resist [41, Figure 15(b)], where the isolated and grouped lines print at the same dimension. This negative resist is currently being used in the fabrication of all 0.35- μm CMOS devices and is commercially available from the IBM/Shibley Deep-UV Resist Alliance. The excellent resolution of an advanced version of CGR is shown in **Figure 7**, where 200-nm resolution has been achieved using a Micrascan® 248-nm exposure tool with 0.5 NA.

While the differential solubility in CGR is achieved through a cross-linking reaction, new chemistry approaches to acid-catalyzed “deprotection” may lead to interesting negative-resist systems [44].

3. Negative resists for micromachining applications

The ability to machine small parts using silicon etching or pattern electroplating is of growing interest in the electronics industry, where it can be applied to the future miniaturization of magnetic disk drives, electron-beam columns, semiconductor test probes, sensors, waveguides for optical networks, and field-emission tips and light modulators for display technologies. Many of these applications require high-aspect-ratio lithography (thickness/resolution) using thick resist films ($>50 \mu\text{m}$) to provide stencils with excellent dimensional control and vertical sidewalls. The best-known technique for forming these high-aspect-ratio structures is a LIGA (Lithographie, Galvano-formung, Abformung) process [45] in which a thick film (up to 1 mm) of PMMA is patterned using a

synchrotron X-ray source. Since this is an expensive, time-consuming process with limited exposure tool availability, it would be desirable if possible to use optical lithography tools and associated commercially available photoresists. Recently several authors have reported on the use of negative photosensitive PWB resists and polyimides [46, 47] and positive diazo-type photoresists [48–51]. While these systems are useful for some applications, it is generally difficult to achieve high-aspect-ratio patterns because of 1) the resolution limitations of thick PWB resists, 2) the high optical absorption of typical semiconductor resist systems, and 3) the difficulty in producing coatings thicker than 50 μm . New resist systems designed specifically for micromachining applications are required which can be spin-coated to achieve thick films that have excellent sensitivity, high resolution, low optical absorption, thermal stability, and chemical resistance.

Epoxy materials are attractive candidates for this application because they are available in a wide variety of molecular weights at low cost. As stated previously, work in the early 1980s reported that epoxy resins could be cationically polymerized by using a photoinitiator such as an onium salt, which generated a strong acid upon exposure to ultraviolet light [24].

One material that looked very promising for this micromachining application [52, 53] was a multifunctional epoxy derivative of a bis-phenol-A novolac (SU-8), which had previously been used to provide the high-resolution patterning for semiconductor devices described in a previous section. This material has the highest epoxide functionality commercially available (Formula VI); when formulated with a commercially available triaryl sulfonium salt as photoinitiator (CYRACURE[®] UVI from Union Carbide), coated on a substrate, and exposed to ultraviolet light (365 to 436 nm), the epoxy resist will form a highly structured cross-linked matrix. In addition to the exposure sensitivity and the excellent adhesion of epoxy derivatives, this resist system has three important attributes which make it very suitable for thick-film applications. First, because of its low molecular weight of ~ 7000 (± 1000), SU-8 can be dissolved in a variety of organic solvents such as propylene glycol methyl ether acetate (PGMEA), gamma-butyrolactone (GBL), or methyl iso-butyl ketone (MIBK) to provide solutions containing up to 85% solids by weight. Thicknesses of 200 μm can be obtained with a single spin-coating. Second, this material has a very low optical absorption in the near-UV; **Figure 8** compares the optical absorption of SU-8 with a typical diazo-type resist system and a dry-film RISTON[®] resist system from DuPont. Owing to this high transparency, aspect ratios of 14:1 have easily been obtained [54], as seen in the scanning electron micrograph in **Figure 9**. Third, because of its

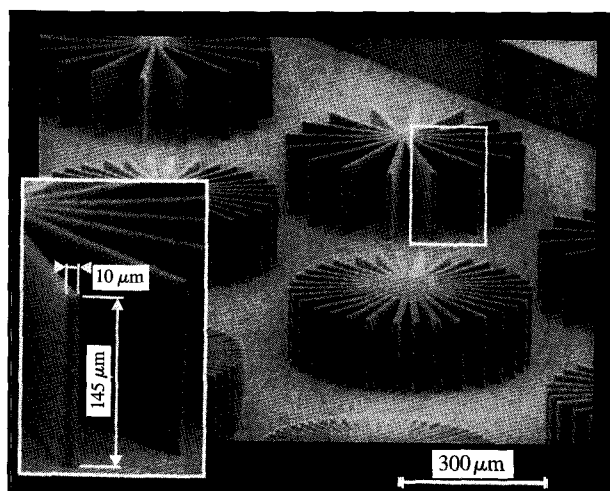


Figure 9

Scanning electron micrograph of 14:1 aspect ratio of SU-8 (reproduced from Reference [57] with permission).

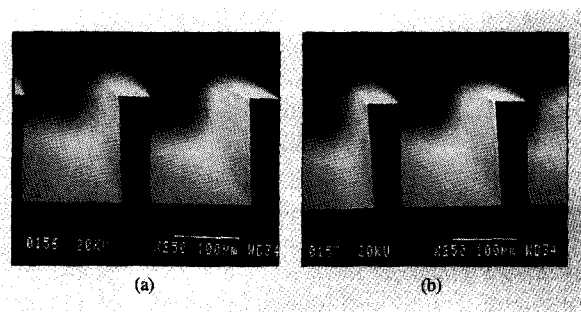


Figure 10

Thermal stability of 165- μm -thick SU-8 images on silicon: Post-baked at 95°C for one hour and subsequently baked at (a) 150°C, one hour; (b) 200°C, one hour.

aromatic functionality and highly cross-linked matrix, the exposed resist is thermally and chemically stable, making it more suitable for the prolonged plasma etching and electroplating processes than PMMA materials. **Figure 10** shows the thermal stability of the patterned structures.

This system has been used to fabricate a variety of high-aspect-ratio microstructures for microelectromechanical (MEM) applications. To fabricate an advanced IBM electron-beam microcolumn [55], miniature octupole lenses are required to deflect and scan the electron beam. Both silicon and gold micro-octupoles were fabricated by using the high-aspect-ratio SU-8 structures as a plasma-

resistant stencil to etch silicon, and as a plating mask to electroplate gold [56]. Also, another recent application has been in the fabrication of micromotors [57].

For certain MEM applications, the use of SU-8 resist provides a low-cost, easily implemented alternative to the LIGA process. While the film thicknesses are currently limited to 200 μm , near-UV patterning of up to 500 μm is anticipated in the near future. Also, the solvents used to strip the SU-8 stencil are not always compatible with the composition of the substrate, and research is continuing to provide high-resolution negative systems that are more easily removed.

Conclusions

Tremendous advances have been made in the development of negative-resist systems since they were introduced in the early 1960s. Their sensitivity, ease of chemical modification, and low cost have made them the materials of choice for the PWB industry; and they are being continually improved to provide greater resolution, ease of processing, and improved physical and thermal properties. For the semiconductor industry, it has been necessary to provide negative resists to meet the ever-increasing circuit density requirements for every new generation of semiconductor devices. Improvements in cross-linked resists have eliminated the swelling seen in early resist systems, and have provided the highest-resolution systems to date. Currently, negative resists based on acid-catalyzed cross-linking are used to fabricate the critical 0.35- μm level of advanced CMOS chips, where linewidth control is key to performance. This is due both to the wider processing latitude of the resist and to the ability to pattern this critical level using a dark-field mask to reduce scattered light reflections in the optical exposure tool lens and in the resist film itself. Work is in progress, both to improve similar systems and to provide new chemistry choices, since the many lithographically patterned levels of circuitry may require both positive and negative systems. Future 193-nm optical exposure tools are currently under development to provide devices with gate widths smaller than 0.2 μm . Current resist systems are too optically absorbing at 193 nm, so incremental improvements in these systems will not achieve future resolution requirements. Totally new resist chemistry and processes must be developed.

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Jane M. Shaw IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598 (shaw@watson.ibm.com). Ms. Shaw is senior manager of the Materials and Processes group at IBM Research in Yorktown Heights, New York. Since she joined IBM at the Thomas J. Watson Research Center, her research has been focused on new fabrication techniques, lithographic materials, polymer materials, metallization, and interconnection technology for chip and packaging applications. Her contributions to lithography include the development of photoresist modeling techniques, the fabrication of new radiation-sensitive polymers, and a metallization process, silylation, which was used to fabricate all of IBM's bipolar logic chips. She has given many invited papers, has organized and chaired sessions at international conferences, and has given short courses for SUNY, the University of California at Berkeley, and the American Vacuum Society. Ms. Shaw has published more than 60 papers and three book chapters; she has 38 patents and 29 technical disclosures in the area of polymer materials and processes for the semiconductor industry. In 1990 she was appointed to the IBM Academy of Technology. Ms. Shaw currently serves on the External Advisory Board of the NSF Science and Technology Center for High Performance Polymeric Composites and Adhesives at Virginia Polytechnic Institute, and on the Industrial Advisory Board of the Massachusetts Institute of Technology Materials Processing Center. She is also a member of the Industrial Advisory Board for Environmentally Conscious Manufacturing at Michigan State University, serves on the IEEE Committee on Environment, Health and Safety, and is a member of the technical working group of the National Electronics Manufacturing Institute for the 1996 Technology Roadmap. Ms. Shaw was named an IEEE Fellow in 1996, and is a member of the IEEE and the MRS.

Jeffrey D. Gelorme IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598 (gelorme@watson.ibm.com). Mr. Gelorme is a research staff member and manager of the Applied Polymer Technology group at the IBM Thomas J. Watson Research Center. He received an M.S. in polymer science and engineering from the University of Massachusetts, Amherst, in 1980. Since joining IBM in 1982, he has been involved in the formulation and development of new photosensitive polymer materials for use in advanced electronic packaging vehicles and in printed circuit board manufacturing processes. Resist materials developed in his group are used throughout IBM and include a high-resolution negative resist used to manufacture 0.5- μm CMOS logic chips, and a low-stress photosensitive polyimide used to develop advanced multichip ceramic module (MCM-D) products. Mr. Gelorme is a member of the American Chemical Society.

Nancy C. LaBianca IBM Research Division, Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598 (ncl@watson.ibm.com). Ms. LaBianca is a staff engineer in the Applied Polymer Technology group at the Thomas J. Watson Research Center. She joined IBM in 1988, working to develop gate metal processes for GaAs technology. She then joined her current group, where she has contributed to a broad range of lithographic activities, including high-resolution photosensitive polyimides for advanced multichip packaging, and the current negative resist, CGR, that is used in manufacturing IBM logic chips. She is currently involved in the imaging of very thick films for micromachining applications; her work in this area has been published and presented at the SPIE and the ECS. Ms. LaBianca is a member of the International Society of Photo-Optical Instrumentation Engineers (SPIE).

Will E. Conley IBM Microelectronics Division, East Fishkill facility, Route 52, Hopewell Junction, New York 12533 (WCONLEY@FSHVM1, wconley@vnet.ibm.com). Mr. Conley joined the IBM East Fishkill Development Laboratory in 1981. He holds more than 20 patents and has published more than 50 papers in the area of lithographic materials and processes. He is currently assigned to the CMOS advanced lithography development team, where he works on front-end critical-level process development for IBM's advanced device program. Mr. Conley is currently the vice-chairman of the SPIE Conference on Advances in Resist Technology and Processing; he is president-elect of the Society of Plastics Engineers of the Mid-Hudson Valley in New York.

Steven J. Holmes IBM Microelectronics Division, Burlington facility, Essex Junction, Vermont 05452 (SHOLMES@BTVLABVM, sholmes@vnet.ibm.com). Dr. Holmes is a photolithography development engineer in the Emerging Technologies Department. He received a B.S. in chemistry from Yale University in 1979, and a Ph.D. in chemistry from M.I.T. in 1983. After postdoctoral studies at Purdue in organic chemical synthesis, he joined IBM at its Essex Junction, Vermont, semiconductor development facility. Dr. Holmes has worked on DUV resist and applications development since that time, with projects including 1Mb and 16Mb DRAM development, logic gate conductor and logic local interconnect lithography. He is currently working on lithography development for sub-quarter-micron logic and memory applications.