Photoresists for 193-nm lithography

by R. D. Allen
G. M. Wallraff
D. C. Hofer
R. R. Kunz

Photolithography using 193-nm light appears to be a viable route for the extension of optical lithography to the dimensions required for the manufacture of 1Gb DRAM and advanced CMOS microprocessors with 180–140-nm minimum feature sizes. In this paper, we discuss the origin of resist technology for 193-nm lithography and the current status of 193-nm photoresists, focusing on single-layer resist materials. We emphasize the photoresist design approaches under investigation, compare these with deep-UV (DUV) (248-nm) resist design and materials, and consider possible future lithography processes employing 193-nm lithography. Research and development on 193-nm photoresists by the lithography group at the IBM Almaden Research Center is highlighted.

Introduction

Explosive growth in the performance of semiconductor devices has been made possible by advances in microlithography and photoresist technology. Today most DRAM manufacturers have committed to the use of high-numerical-aperture (NA ~ 0.6) optical lithography, at a wavelength of 365 nm (referred to as "365-nm lithography") for 350-nm (16Mb) products, while a trend toward the use of 0.5-NA, 248-nm lithography for microprocessor critical levels appears to be in progress. A number of companies in the industry have had R&D-level experience with 0.50-NA, 248-nm lithography and now appear focused on the idea of using 0.60-NA, 248-nm lithography to manufacture 250-nm product, but are anxiously awaiting the availability of the 0.60-NA tools required. The next horizon is 180-nm CMOS technology required for 1Gb DRAM and advanced microprocessors.

Why extend DUV lithography from 248 to 193 nm?

The industry is facing several important questions: *"Can one manufacture 180-nm (minimum feature size) product with 0.60-NA, 248-nm lithography?"* If not, *"Can this product be manufactured with 193-nm lithography and can one consider the possibility of manufacturing at dimensions of 0.15 μm using 150-nm photolithography, or should the industry consider a change to an alternate technology such as EUV (extreme-UV, also known as soft-X-ray), e-beam, or X-ray lithography?"* Without attempting to provide an answer to these global questions, let us consider the benefits derived from the shift from 248- to 193-nm lithography.

Many state-of-the-art photoresists now function at a Rayleigh k_1 value of 0.50 under conventional illumination with chrome-on-glass masks. These resists are said to be "linear" to a minimum feature size of $\lambda/2(NA)$, with exposure latitude of ±10%, or 250 nm (0.25 μm) in the case of 248-nm lithography at 0.50 NA. While it is possible to fabricate development-level devices under these conditions, the total process window afforded under these circumstances is rarely adequate to manufacture semiconductor product in high yield. Hence, "optical enhancements" such as off-axis illumination and/or phase masks are required to make this lithographic system (comprising tool and resist) function with a process window commensurate with manufacturing requirements.

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Table 1 Lithography-resist process options.

Process	*Dimension* (μm)
SLR 248 resist SLR 248 resist, optical enhancements BL/TSI 248 resist BL/TSI 248 resist, optical enhancements SLR 193 resist	0.25
SLR 248 resist, optical enhancements BL/TSI 248 resist, optical enhancements SLR 193 resist BL/TSI 193 resist BL/TSI 193 resist, optical enhancements	0.18
SLR 193 resist, optical enhancements BL/TSI 193 resist, optical enhancements	0.14

It is thus likely that the transition from 248- to 193-nm lithography will depend largely on the trade-offs among the cost/performance of 248-nm, 0.6-NA optically enhanced lithography, conventional 193-nm, 0.6-NA lithography, and "optically enhanced" 193-nm, 0.6-NA lithography.

If the semiconductor industry ultimately has available 0.6-NA exposure tools, optical enhancements, and both single-layer resists (SLR) and bilayer resists or top-surface imaging (BLR/TSI) resists at 248 and 193 nm, numerous resist/lithography technology choices will be available for the 0.25–0.15-μm device generations. These choices are listed in **Table 1**. While it is difficult at present to determine which of these options will be chosen for each of the next three generations of semiconductor manufacturing, it is possible that the current need for higher levels of integration and performance in microprocessors and DRAM will lead to economic feasibility for 0.25–0.15-μm manufacturing.

If history is any guide, and if the economics of manufacturing permit, the answer to the question *"Why switch to 193-nm lithography?"* may be the following:

1. 193-nm lithography offers the possibility to extend DUV lithography with optical enhancements to 0.15-μm dimensions, and possibly to smaller dimensions.
2. "Mild" optical enhancements of 193-nm lithography are likely to afford manufacturable lithographic processes at 0.18-μm dimensions.
3. Backward introduction of 193-nm lithography to 0.25–0.18-μm device manufacturing would afford low-cost, conventional DUV processes without optical enhancements.

A number of factors including the considerations discussed above will lead to 21st-century semiconductor manufacturing facilities (fabs) that differ considerably from present facilities. First, the size of high-performance microprocessor and DRAM chips may help to stimulate a switch from standard step-and-repeat lithography systems to step-and-scan systems. The economies of scale, the cost of lithography tooling, and the need for economical high-precision single-wafer processes, especially in plasma (dry) processing, will lead to the introduction of 12-in. "dinner plate" wafers to replace the present 6-in. and 8-in. wafers. The lithography systems will all likely utilize chemically amplified photoresists which, unless unusual advances are made in providing resistance to airborne contamination, will require chemically filtered air enclosures for both steppers and process wafer tracks. The financial need to carefully optimize lithographic productivity and reduce the new capital tool investment per generation could well lead to 1Gb DRAM or microprocessor fabs containing a multiplicity of lithographic tools. Such tools could include combinations of steppers and scanners, large-field, 365-nm (I-line) tools for the larger feature levels, 248-nm DUV tools for 0.25–0.35-μm (and larger) features, and finally 193-nm tools for critical 0.18-μm levels (and below), as well as patterning of 0.25-μm features without the expense of phase mask utilization. Finally, difficult critical levels such as deep isolation trench, if they are still a part of advanced CMOS technology, will likely require the use of top-surface-imaged lithography, including fully integrated exposure, silylation, and RIE systems, to achieve the resist aspect ratios required for demanding plasma processes. Thus, once 193-nm lithography has advanced to the semiconductor fab, it will be utilized for a number of generations in both single-layer and bilayer/TSI forms (first at critical levels, later for other levels).*

Single-layer resist (SLR) approaches

The high-volume manufacture of semiconductors today involves the exclusive use of single-layer-resist (SLR) processes, although potentially higher-performance top-surface-imaged (TSI) and bilayer (BL) photoresist systems have long been proposed as alternatives [1, 2]. These resist processes, depicted in **Figure 1**, may be distinguished by their complexity, with the number of process steps increasing considerably in the progression from SLR to BL and TSI approaches. As a consequence, the relative simplicity of the single-layer-resist approach has always been preferred as long as the desired products are manufacturable. This is the main driver to shorter wavelengths and new photoresist materials and imaging mechanisms. The semiconductor industry will extend the use of optical lithography with single-layer-resist processes

*At a recent ARPA 193-nm lithography program, Shaver of MIT Lincoln Laboratory pointed out that "... the last optical lithography will be around for many years, even if not for critical levels."

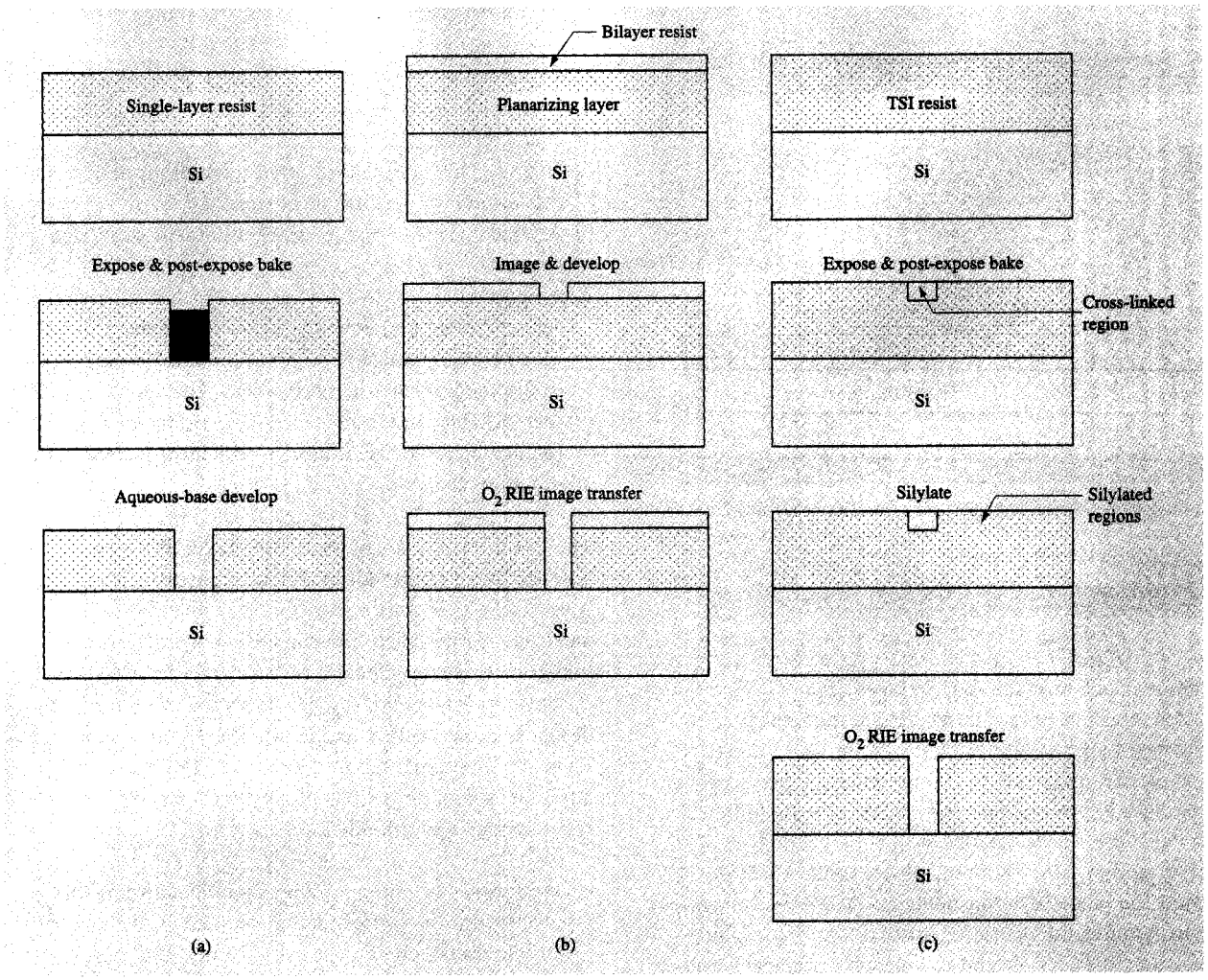

Figure 1

(a) Single-layer, (b) bilayer, and (c) top-surface-imaged TSI resist processes.

as far as possible. When DUV lithography (either 248- or 193-nm) must be extended to performance limits that exceed the capability of single-layer resists, thin imaged resist systems (either TSI or BL) will likely emerge as important high-end manufacturing processes.

It would indeed be fortunate if the transition from 248- to 193-nm lithography could occur in a relatively smooth manner, like the transition from 436 to 365 nm in the late 1980s. Many 436-nm (G-line) photoresists functioned effectively at 365 nm (I-line) because both the optical properties and the photochemistry of the diazonaphthoquinone/novolak photoresists were similar at these wavelengths. However, this was not the case in the very difficult subsequent transition from 365-nm lithography to 248-nm imaging. Both the materials and the imaging mechanism (including photochemistry) were necessarily changed completely with the introduction of chemical amplification (CA) (in the form of an acid-catalyzed deprotection chemical reaction) [3].

The degree of difficulty in the transition to 193-nm lithography falls somewhere between these past two lithography transitions. The optical properties of the current 248-nm DUV resists are very different at the 193-nm exposure wavelength. The optical absorbance of a typical p-hydroxystyrene-based DUV resist is shown as a function of wavelength in **Figure 2**. At a wavelength of 193 nm, the 0.3 absorbance per micron of a 248-nm resist increases to more than 10 per micron. At this high absorbance, 193-nm radiation cannot penetrate through to the bottom of a 248-nm resist layer, rendering

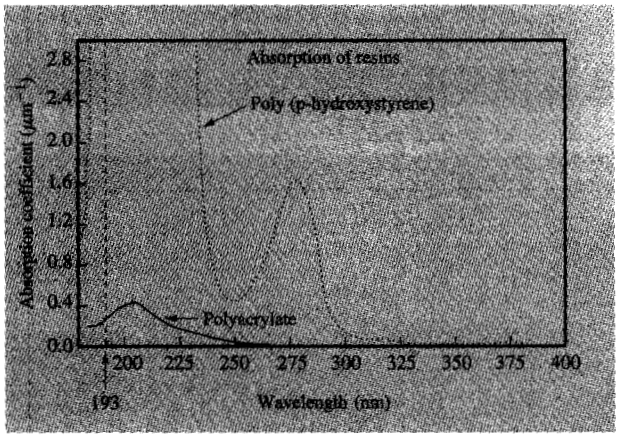

Figure 2

Ultraviolet absorbance spectra of DUV resist polymers: Dotted curve, phenolic polymer (248-nm resist); solid curve, acrylic polymer (193-nm resist).

commercially available DUV resists useless for exposure at 193 nm. The acid-catalyzed chemical amplification chemistry used in commercial 248-nm DUV resists is completely applicable to 193-nm imaging, however. One complication in this imaging chemistry is the difference in chemical reaction pathways for the generation of photoacid at these different wavelengths, which is discussed below. The introduction of 193-nm lithography thus requires the development of a family (or families) of photoresist materials and chemistries specifically tailored to function at this wavelength.

A high-performance single-layer photoresist is needed for the successful introduction of 193-nm lithography for a number of reasons: First, a simple lithographic process must be available to develop 193-nm DUV lithography exposure tools. Second, industry acceptance of a new lithography wavelength is likely to be most effective when SLR processing accompanies the new lithography. Finally, 193-nm lithography will probably replace 248-nm lithography when and if the replacement is economical and provides significant improvement in chip performance (or manufacturing yield). Consequently, new 193-nm single-layer resists with high-performance imaging characteristics (resolution, depth of focus, process latitude, adhesion, sensitivity), plasma etch resistance equivalent or even superior to conventional DUV resists, and compatibility with industry-standard processing chemicals (aqueous-base developers) must be developed.

New polymer materials with high optical transparency are required for 193-nm (single-layer) resists. This optical transparency at the exposure wavelength must be combined with a set of properties possessed by hydroxystyrene polymers, which are the standard building block primarily of conventional DUV (248-nm) resists:

1. Hydrophilicity (for good positive-tone development characteristics).
2. High T_g (130–170°C), for good thermal properties and the latitude to perform higher post-exposure bakes.
3. Aromatic rings in high concentration (for good etch resistance).
4. An easily blocked hydroxyl group [for incorporation of acid-cleavable functionality, i.e., a functional group which is easily attached to an acidic moiety such as a carboxylic acid that is reactive and removable (deblockable) in the presence of a strong (photogenerated) acid, thereby providing a significant solubility change].

These four characteristics are often taken for granted because they are present by default in hydroxystyrene-based DUV (248-nm) resists, but they must be painstakingly designed into single-layer resists for 193-nm lithography, where phenolic resins cannot be used.

Acrylic polymers are the new basis for 193-nm resist design because of their excellent optical transparency (see Figure 2) and easily tailored structure. The characteristics, advantages, and limitations of acrylic chemically amplified resist systems are listed below:

- *Transparency at 193 nm* The aliphatic nature of the polymer and the low extinction coefficient of the vibronic transition (λ_{max} at 210–220 nm) are characteristics of a very transparent polymer. Figure 2 shows a comparison of the absorbance properties of poly(4-hydroxystyrene) (PHOST) with poly(methyl methacrylate) (PMMA).
- *Property diversity* Substitution of the ester "R" group permits great flexibility in modifying polymer properties. Additionally, copolymerization can dramatically expand the property spectrum. A virtually infinite variety of polymer characteristics can emanate from this family. Fortunately, the optical transparency at 193 nm is virtually 100%, providing an excellent platform on which to build a resist.
- *Ease of synthesis* Acrylic polymers prepared for 193-nm single-layer resists are products of a direct synthesis, unlike traditional DUV polymers, which are made via a two-, three-, or even four-step process, adding significantly to complexity and cost of preparation. In another departure from DUV materials, acrylic polymers are synthesized without the need for acids or bases. In short, resist component manufacturability, an enormous impediment to the move to DUV (248-nm) technology, may not be nearly as problematical in 193-nm SLRs.

- *Plasma etch resistance* Simple acrylics have etch rates in aggressive plasma environments found in many semiconductor processes that are approximately twice those of phenolic resists. Therefore, the polymer must be substantially modified to provide suitable etch resistance.

Three key breakthroughs in the development of acrylic-based resist chemistry prior to the recent worldwide efforts toward the development of a 193-nm SLR [5] were

- Development of acid-catalyzed deprotection chemistry (chemical amplification) in the early 1980s, including acid-catalyzed reactions of esters of methacrylic acid by Ito and coworkers at IBM [4].
- Development of all-acrylic, aqueous-developing positive resists employing the methacrylate terpolymer concept, by IBM in the late 1980s [5].
- Recognition by workers at Fujitsu that plasma etch resistance and 193-nm transparency can reside simultaneously in an acrylic resin through incorporation of alicyclic components [6].

No other polymer type has to date been demonstrated to possess the combination of properties required for resist design at 193 nm. In the next section, we discuss the various approaches currently under investigation, most of which involve acrylic backbones. We describe in some detail one of the first 193-nm resists which was developed for use in exposure tool evaluation (IBM Version 1 Photoresist), and a first-generation etch-resistant photoresist (IBM Version 2). We briefly discuss the impact of the shift from 248 nm to 193 nm on substrate reflectivity considerations and on photoacid generator (PAG) photochemistry.

- *Tool evaluation resist*

The first high-speed, high-resolution positive single-layer resist was developed in 1993 by the IBM/MIT Lincoln Laboratory team [7]. The primary purposes of this (IBM Version 1) resist were to evaluate the imaging performance of the SVGL (Silicon Valley Group, Lithography) prototype 193-nm step-and-scan system, and to demonstrate the feasibility of a 193-nm SLR. To properly evaluate a new tool, it was of the utmost importance to design the Version 1 resist with dual-wavelength (193-, 248-nm) capability. With this design, the resist can be exposed with a 248-nm stepper with known characteristics, and questions about stepper (optics) quality and resist performance are separable.

The Version 1 resist (**Figure 3**) comprises two components, an iodonium triflate onium salt and a methacrylate terpolymer originally developed for printed-circuit-board lithography [5]. Each monomer serves a

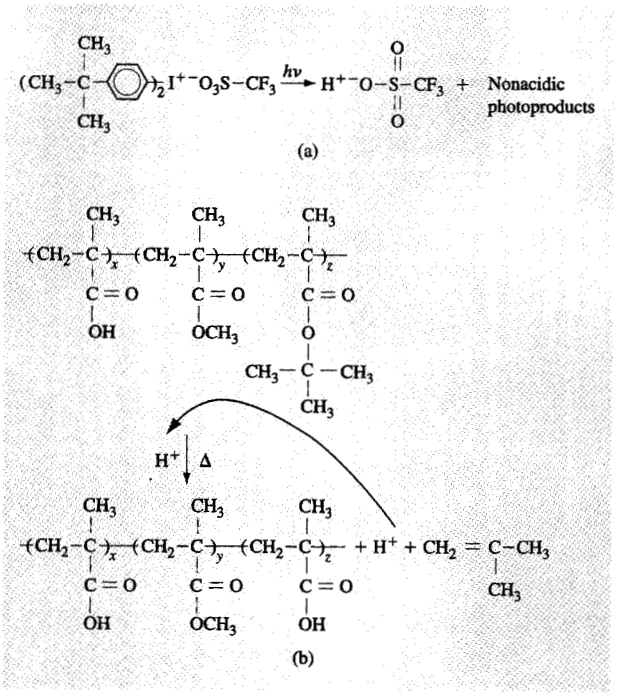

Figure 3

Chemical structure of 193-nm single-layer IBM Version 1 resist: (a) PAG; (b) methacrylate terpolymer.

separate function in the terpolymer. T-butyl methacrylate (TBMA) provides an acid-cleavable side group which is responsible for creating a radiation-induced solubility change. Methyl methacrylate (MMA) promotes hydrophilicity for photoinitiator solubility and positive-tone development characteristics, while also improving adhesion and mechanical properties and minimizing shrinkage after exposure/bake processing steps. Methacrylic acid (MAA) controls aqueous development kinetics. This polymer is prepared in a single step from readily available, inexpensive components. By selecting the terpolymer composition and molecular weight, imaging properties (such as dissolution properties, photospeed, contrast) can be altered to a significant extent.

Version 1A (initial formulation) resist was used extensively on the SVGL Micrascan® 193 prototype. In fact, the resist was integral to the optical characterization of the tool and accelerated optimization of the prototype's optical characteristics. The highest resolution obtained at 193 nm (NA = 0.5) for Version 1A was 0.22 μm in 0.75 μm of resist. **Figure 4** shows 193-nm imaging of this resist using the SVGL prototype step-and-scan system.

An advanced version of this resist (Version 1B) was developed in 1994. Version 1B has been used principally on the GCA (XLS) 248-nm stepper at MIT Lincoln

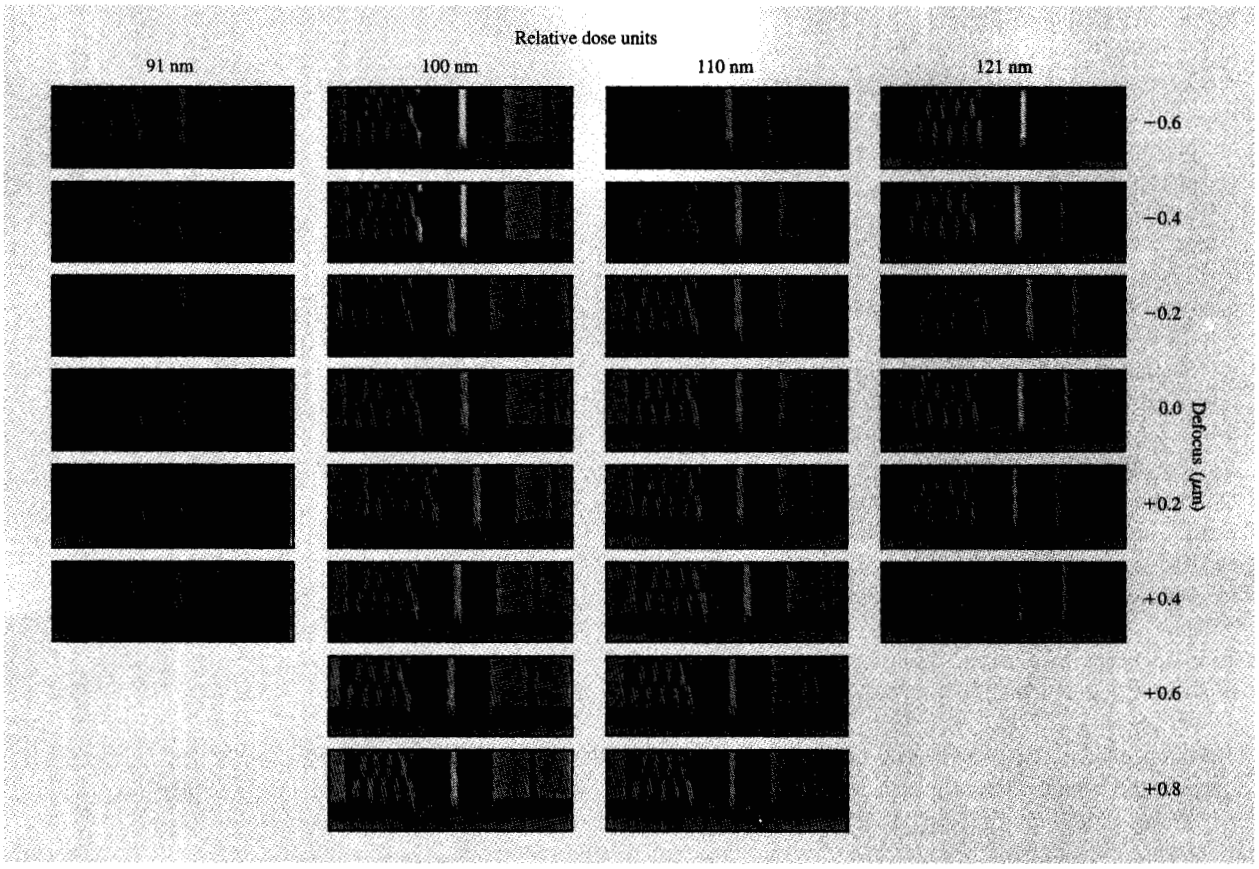

Figure 4

Single-layer Version 1 resist with 193-nm lithography: 0.25-μm features exposed on Micrascan 193 (100 dose units ~ 20 mJ/cm^2).

Laboratory. The resist is linear to 0.30 μm at a resist thickness of 0.75–0.85 μm with good process latitude, and is able to resolve features down to 0.25 μm with this DUV stepper when overexposed. **Figure 5** shows the resolution capability in Version 1B exposed with this 248-nm stepper at dimensions of 0.30 μm, pictured through a dose range of 5.2–6.4 mJ/cm^2. Recent imaging results with 193-nm exposure show a further gain in resolution to 0.14 μm.

It should be noted that most of the acrylic-based resists develop with base (hydroxide) concentrations (0.01–0.05N) significantly lower than are typically used with the current production concentrations (0.21–0.26N) of phenolic (248- or 365-nm) resists. This difference could affect the introduction of this class of 193-nm resists into a manufacturing environment.

• *Etch-resistant resists*

The Version 1 resists described above have etch properties surprisingly similar to those of conventional DUV resists (e.g., IBM APEX-E) in CF_4-based (oxide) etch recipes. More aggressive etch chemistries (e.g., aluminum and polysilicon etching) demand substantial increases in etch resistance. For example, the etch rate of the Version 1 resist can be three times as high as that of a novolak-based resist under halogen etch conditions used widely in the semiconductor industry. The approach currently being used to impart etch resistance without degrading the optical transparency of 193-nm single-layer resists involves incorporation of alicyclic (aliphatic/cyclic) compounds into the polymer structure.

The etch resistance of acrylic resists can be substantially improved by increasing the carbon content of the polymer via the incorporation of cyclic aliphatic functionality. For example, the etch rate of poly(isobornyl methacrylate) is less than half that of poly(methyl methacrylate) in a hydrogen bromide plasma [6]. This approach is based on earlier studies which correlated the etch rate with the carbon/hydrogen ratio of a series of polymers [8]; it is currently the method most commonly used to develop etch-resistant, transparent 193-nm photoresists.

It is apparent from published resist approaches that high-resolution lithography using a 193-nm SLR is possible. It is equally likely that plasma etch resistance approaching DUV aromatic resists is feasible. Much less certain is the development of a resist formulation which possesses a combination of both imaging quality *and* plasma etch resistance. The lack of flexibility in a traditional resist design approach, coupled with the often competing considerations of hydrophilic–hydrophobic balance, lithographic contrast, high T_g, thermal stability, and etch resistance, limits the options of the 193-nm resist designer.

To provide greater flexibility in resist design, we have developed three-component resists consisting of a *methacrylate polymer* slightly modified from Version 1, an *alicyclic dissolution inhibitor* compound, and finally, a *photoacid generator*. After evaluation of large numbers of dissolution inhibitor compounds, it became apparent that a class of compounds (5-*B* steroids) was available (from natural sources) with the following very desirable properties:

- High solubility in resist and PGMEA.
- Strong dissolution inhibition.
- High exposed dissolution rate.
- 193-nm transparency.
- Moderating influence on T_g.
- Plasma etch resistance.
- Good thermal stability (>200°C).

This three-component approach (IBM Version 2) (**Figure 6**) offers flexibility for both tuning resist performance and realizing increased etch resistance simultaneously. The etch resistance of Version 2 resist is far better than that of Version 1. The presence of alicyclics in *both* the polymer and dissolution inhibitor produced chlorine etch rates only slightly faster than novolak resins. Version 2 resist has achieved etch rates 1.2 times that of traditional DUV resists, in a resist formulation with good imaging quality. **Figure 7** shows an example of this combination of properties, as exposed at 248 nm on the GCA XLS stepper. This is perhaps the first example of the *combination* of etch resistance and imaging quality in a non-phenolic, 193-nm-transparent photoresist.

- *193-nm wavelength effects on photoacid generator efficiencies and substrate reflectivity*

In addition to the polymer transparency issues, the primary impact of the switch from 248 to 193 nm on the design of CA resists involves resist chemistry, specifically related to the photoacid generator (PAG). The effect of the change in exposure wavelength is confined to photochemical processes, since the thermal acid-catalyzed reactions occurring in CA resist are independent of

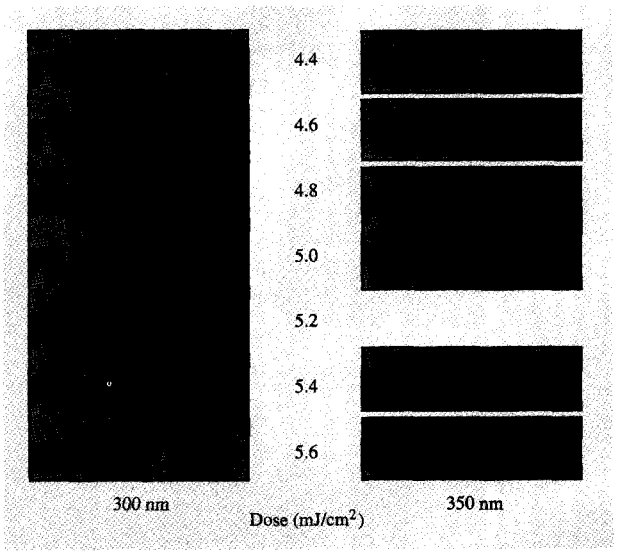

Figure 5

Single-layer Version 1B resist with 248-nm lithography: 300-nm and 350-nm features printed through a range of exposure doses using a GCA XLS 0.48-NA DUV tool.

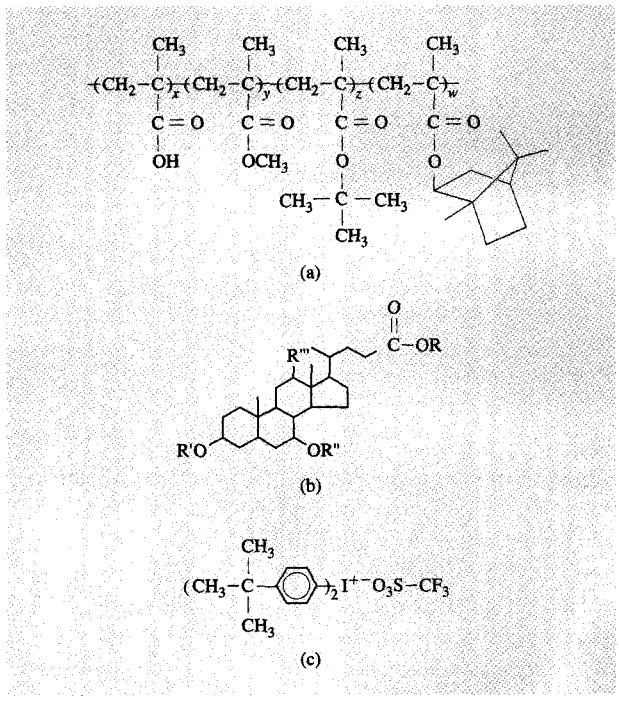

Figure 6

Chemical structures of 193-nm single-layer IBM Version 2 resist: (a) methacrylate tetrapolymer, (b) steroid dissolution inhibitor, and (c) PAG.

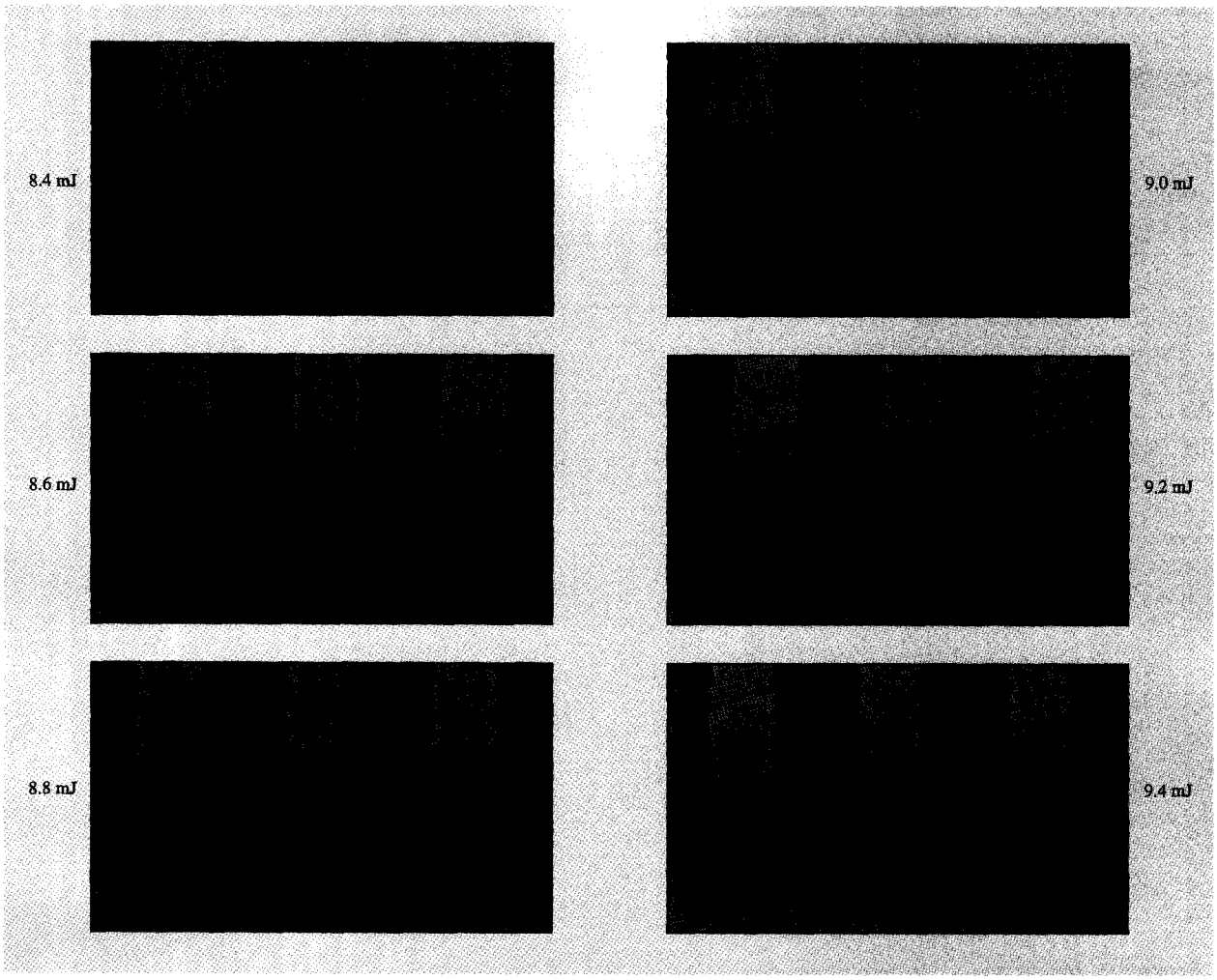

Figure 7

Version 2 resist with 248-nm lithography: 300-nm features printed through a range of exposure doses using a DUV 0.48-NA stepper ($\sigma = 0.55$). Note: Etch rate in chlorine plasma ~ 1.2× APEX-E.

exposure wavelength. Although the significantly higher photon energy at 193 nm compared to 248 nm [6.42 eV (148 kcal/mol) vs. 4.89 eV (115 kcal/mol), respectively] opens the possibility of new photochemical pathways for the polymer matrix (i.e., scission of the polymer backbone, as seen in PMMA resists), it is likely to be relatively insignificant because of the *low doses employed in CA resist systems*. Of greater importance will be the availability of PAGs which are efficient photoacid generators at 193 nm. Ideally, one would like to use the same PAG materials which were developed for 248-nm applications. It appears (with the exception of the PAGs whose photochemical mechanism of acid generation relies on photoinduced electron transfer sensitization with a phenolic polymer matrix) that most of the PAGs developed for 248-nm lithography will function at the 193-nm wavelength. Transparency problems can arise, however, because of the aromatic nature of most PAGs. Recently, more transparent PAGs have been specifically developed for 193-nm resists [9].

In summary, it seems that while only a subset of DUV 248-nm PAGs can be used at 193 nm, these compounds, coupled with new PAGs which are being developed, should provide a material set diverse enough for the formulation of 193-nm chemically amplified resists.

The evolution from 365 to 248 nm has presented lithography engineers with new challenges caused by increased thin-film interference effects in resists during

exposure. These challenges were the result of the inherently higher reflectivity which occurs at shorter wavelengths and the development of new nonbleachable photoresists, and have fueled the development of both top- and bottom-antireflective-layer (ARL) technology for use at 248 nm. The extension of production photolithography to 193 nm will also require reflection suppression for certain lithography levels. Extensive experimental and modeling work has already been done at 248 nm to better understand requirements, limitations, and performance of ARL technology [10]. This framework will have a direct bearing on developments at 193 nm, since much of this modeling can be generically applied to any exposure wavelength. The limitation at 193 nm, however, lies in knowledge of the optical properties of the materials in use, since few commercially available instruments can measure the complex refractive index at wavelengths of less than 200 nm.

Most bottom ARLs designed for use at 248 nm are composed of strongly absorbing phenyl-containing polymeric systems; as was noted above, these materials are less than ideally suited for 193-nm exposure. These very high absorptivities lead to reflection coefficients at 193 nm that, although small (2–5%), are several times higher than reflection coefficients at 248 nm. However, prototype 193-nm ARLs have already been developed which incorporate a more transparent methacrylate functionality [11] and have refractive indices of 1.5–1.6. These ARLs better match the real part of the refractive index of the 193-nm resist systems, which are also methacrylate-based. From these early experiments, it seems that 193-nm ARL development should be considerably easier than development of the corresponding single-layer resists, and such development should be limited only by the availability of precision measurement tools at 193 nm.

Resists for 193-nm lithography: Summary and challenges

In this discussion, we have concentrated on the IBM Research activities in collaboration with MIT Lincoln Laboratory. In the past twelve to eighteen months, there has been a dramatic worldwide increase in the development activities in many areas of 193-nm resists. The following subsections are references to some of this work.

New polymers Workers at IBM, in cooperation with the University of Texas and B. F. Goodrich, have demonstrated that 193-nm resists can be developed using (nonacrylic) polymers based on the polymerization of cyclic olefins (e.g., norbornene derivatives) [12]. The imaging properties do not yet approach those of photoresists based on acrylic polymers, but plasma etch rates lower than those of novolak have been demonstrated. Workers at AT&T (Lucent Technologies) have published information on a new resist system that is effectively a cyclic olefin/acrylic hybrid with attractive resist performance [13].

New high-performance resists Workers at Fujitsu [14], NEC [15], and Toshiba [16] have recently published information on new (second-generation) acrylic resists which combine good etch resistance and clearly improved imaging characteristics. Lithographic performance data on 193-nm steppers with these new resists remain to be demonstrated.

Significant challenges face the industry in this era of early research and development of 193-nm resists, especially in the following areas:

- The need for an etch-resistant single-layer resist, compatible with 193- and 248-nm exposure tools, with resolution capability (k-factor) equivalent to the new generation of DUV resist technology.
- Single-layer resists compatible with industry-standard developers (e.g., 0.26N TMAH).
- Alternate polymer families (beyond acrylics) for 193-nm SLRs.
- Negative-tone 193-nm SLRs.
- High-performance, aqueous-developing silicon-containing resists for 193-nm bilayer systems.
- Top-surface-imaging (TSI) resists with faster photospeeds than the current resists.
- Timely development of optical exposure tool infrastructure.

Acknowledgment

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Robert D. Allen *IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120 (rdallen@almaden.ibm.com).* Dr. Allen is a research staff member in the Lithography group at the IBM Almaden Research Center. His research is focused on new resist materials and processes for 193-nm lithography. He received his B.S. in chemistry from Gannon College, Erie, Pennsylvania, and his Ph.D. in polymer chemistry from Virginia Tech.

Gregory M. Wallraff *IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120 (gmwall@almaden.ibm.com).* Dr. Wallraff is a research staff member in the Lithography group at the IBM Almaden Research Center. His research is focused on gaining a greater fundamental understanding of photoresist behavior. He holds a B.S. in chemistry from the College of St. Thomas and a Ph.D. in physical organic chemistry from the University of Utah.

Donald C. Hofer *IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120 (hofer@almaden.ibm.com).* Dr. Hofer is manager of the Lithography group at the IBM Almaden Research Center. He received his B.S. in chemistry and mathematics from Bethel College, South Dakota, and his Ph.D. in physical chemistry from the University of California.

Roderick R. Kunz *Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts 02173.* Dr. Kunz received his B.S. in chemistry from Rensselaer Polytechnic Institute in 1983 and his Ph.D. in chemistry from the University of North Carolina at Chapel Hill in 1988, working at the IBM Thomas J. Watson Research Center in 1987. Since 1988, he has been a staff member in the Submicrometer Technology group at MIT Lincoln Laboratory, where his principal focus has been the development of 193-nm photoresist processes and the investigation of excimer laser direct processes such as deposition and *in situ* patterning. Prior to joining Lincoln Laboratory, Dr. Kunz studied the fundamental aspects of both particle-beam-induced and etch processes.