193 nm Photoresist R&D: The Risk & Challenge

Donald C. Hofer, Robert Allen, Greg Wallraff, Hiroshi Ito, Greg Breyta, Phil Brock and Rick DiPietro
IBM Research Division
Almaden Research Center
San Jose, CA USA
and Will Conley
IBM Microelectronics Division
Fishkill, NY USA

In this paper we examine the technical and business environment in which 193 nm photoresist R&D is conducted today. Semiconductor industry predictions of lithographic requirements for future generations of DRAM and Logic indicate the need for 0.18 and sub 0.18 µm manufacturing capability within the next decade. 248 nm DUV lithography and the tool/photoresist infrastructure is just reaching the state required for manufacturing at 0.25 µm dimensions after a decade of intensive effort at tool and photoresist development. 193 nm tool and photoresist development is beginning to demonstrate potential for 0.18-0.15 µm capability but much progress is required for the 193 lithography infrastructure to reach a the point at which manufacturing capability can be applied to the 1 Gb and later generations of semiconductor technologies. In this paper we will compare and contrast 248 and 193 nm photoresist R&D.

1. Introduction

Current semiconductor industry trends indicate that the development of 1 Gb DRAM and high performance logic processors will require the availability of 0.18 to 0.15 µm lithographic processes in the timeframe of 1998 to 2000 with manufacturing capability at this dimension needed after 2002. Today, only 248 nm DUV lithography is available for these applications but it is expected or more appropriately hoped that manufacturing quality 193 nm tools will be available after 1998. With the anticipation of 193 nm manufacturing tool availability, the challenge for the semiconductor manufacturing industry today is to understand the potential for both 0.6 NA 248 and 193 nm lithography at these dimensions. Finally, another possibility is that higher NA 248 tools (0.65-0.70) could be available in the same timeframe as 193 nm tools. However, simple resolution modeling indicates that the 0.16 µm resolution of a chrome on glass (COG) 0.6 NA, 193 nm resist process provides 193 nm lithography with a slight edge over the 0.18 µm resolution of a 0.7 NA, 248 nm COG process.
Resolution is, however, not the only important consideration in the selection of a lithography process. Process latitude is generally equally as important and so one must consider the depth of focus, exposure latitude and reactive ion etch resistance of the lithography and photoresist materials under consideration. Process latitude has two components, one of which originates from the lithographic tool/mask and the other originates in the photoresist/process. Process latitude resulting from the lithographic tool and mask can be termed optical process latitude while latitude originating from a photoresist and process can be termed resist process latitude. Both of these sources of process latitude will be pivotal in reaching the goal of manufacturable sub 0.18 µm DUV lithographic processes.

Optical process latitude, on a given tool set, can be improved with the use of off axis illumination and phase masks while resist process latitude can be improved by engineering DUV photoresists to provide greater DOF and exposure latitude. Improvements in the DOF for 0.25 µm features with second generation 248 nm DUV resists are examples of this component of process latitude. Note, the first generation commercially available 248 nm resists exhibited approximately 0.6 µm DOF for 0.25 µm l/s features on 0.5 NA tools while the second generation 248 nm DUV resists that are just becoming commercially available exhibit between 0.8 and 1.0 µm DOF for these same features. These single layer resist process latitude improvements alone with COG exposure are unlikely to meet the 0.18-0.15 µm requirements for a number of reasons: 1) Isolated line lithographic performance is a greater challenge than nested line performance. 2) A k2 of 1.0 will result in a 0.6 NA, 248 nm DOF of only .69 µm and at 193 nm a DOF of 0.54 µm. Clearly other means must be sought to realize acceptable process latitude and the increased DOF and it is expected that both off-axis illumination and phase masks will play a significant role in sub 0.18 µm DUV lithography.

2. Lessons from 248 nm DUV Lithography

The first utilization of the concept of chemical amplification in DUV lithography was reported in 1982 by Ito, Wilson and colleagues(1) with the report of high contrast/sensitivity imaging of TBOC protected polyhydroxystyrene resin. Imaging in this resist system was realized with the "super acid" acid catalyzed deprotection of T-BOC styrene produced by DUV photoacid generation from triphenylsulfonium hexafluoroantimonate and thermal activation of the deprotection kinetics. Subsequently, most early chemically amplified DUV resists utilized "super acids" although it was discovered in the late 1980s that lower strength photoacids such as triflic acid sufficed to produce acid catalyzed deprotection of a number of resist chemistries.
The first significant problem with CA type DUV resists was reported in the late 1980s(2,3) with the observation of extensive interruption of chemically amplified chemistry by airborne bases to produce the now well known "t-topping phenomenon". The photoresist industry struggled with this contamination problem for nearly a decade by first utilizing carbon filtration of air in closed wafer trac/exposure tool systems. The most widely utilized commercially available DUV photoresists utilized today are relatively sensitive to the presence of airborne chemical base contaminants and hence, manufacturing use of this product requires the use of activated carbon air filtration for both the wafer trac and stepper housings.

In the early 1990s evidence of significant progress toward a resist design solution to the airborne contamination problem emerged through the invention of CA type chemistry that is largely immune to environmental contamination effects. Two approaches to the realization of immunity to contamination resistance have emerged: 1) The work of Ito and coworkers(4) in which chemistry and process is used to reduce the diffusion coefficient for diffusion of contaminants into the film. The reduction in small molecule diffusion coefficient is achieved by the thermal annealing of the resist film with resultant reduction of the free volume of the film. This approach has been quite successful and has been introduced by Shipley Company as the product XP9549 and is more popularly known as ESCAP (Environmentally Stable Chemically Amplified Positive resist). A second approach to the avoidance of airborne contamination effects first published by Huang and coworkers (5), termed KRS, involved the utilization of low activation energy deprotection chemistry so that deprotection occurred immediately upon exposure before airborne contaminants could diffuse into the resist film. Other research published since the KRS system have expanded on the types of low activation chemistries utilized to include a wide variety of acetal and ketal protecting groups (6, 7). Today, 248 nm DUV resist chemistries abound with a wide variety of hydroxystyrene based copolymers and acid labile protecting groups and photoacid generators(8, 9, 10).

Since the emergence of the DUV resist chemistries cited above, the presumed focus by commercial photoresist suppliers on specific chemical platforms the industry has begun to discover subtleties of specific resist formulations. Some examples of these subtleties include: The contribution of photoacid molecular size to diffusion of acid and the influence of acid diffusion on surface depletion and t-topping (11). The contribution of photoacid pKa and the activation energy for deprotection to the sensitivity of linewidth change to post exposure bake temperature. The influence of acid buffering additives on lithographic performance of a resist, including sensitivity (12). The propensity for low activation energy resists to continue acid deprotection kinetics at room temperature after exposure and the emergence of the "linewidth slimming problem".

The photoresist industry seems to have arrested or reduced to insignificance most of the
problems cited above at this time because a number of companies are supplying 248 nm DUV photoresists to semiconductor companies who are utilizing them in low volume manufacturing successfully. However, at this time the 248 nm DUV photoresist market is quite small but is expected to increase substantially in the next few years. This topic will be discussed in more detail later in this paper.

3. 193 nm DUV Photoresist Materials

The prospect of utilizing 193 nm lithography to extend the potential for UV lithography to sub 0.25 µm dimensions is a recent phenomenon which was first discussed in 1990. At that time high performance DUV resists were not commercially available but the best of experimental resist systems imaged on existing 248 nm excimer tools with 0.5 NA optics exhibited promising 0.25 µm lithography. However, it was clear that lithographic performance at dimensions significantly smaller than 0.25 µm was not likely on these systems. In the same era the first largely reflective 0.5 NA DUV system became available in the form of the MSII. With the expectation that DUV lithography could be extended to dimensions considerably below 0.25 µm with a wavelength shift from 248 to 193 nm, a study of the optical characteristics of materials suitable for the illumination system of a MSII operating at 193 nm was initiated at MIT-Lincoln Labs. The results of this study indicated that glasses with a low enough absorption coefficient at 193 nm to be utilized in a prototype lithography system could be obtained. The first prototype 193 nm step & scan system was delivered by SVGL to MIT-Lincoln Laboratories in late 1992.

At this time a single layer 193 nm DUV resist system had not been reported in the technical literature. A collaborative effort between the IBM Almaden Research Center and MIT-Lincoln Labs was initiated in late 1991 to develop a prototype 193 nm single layer resist for the purpose of providing a photoresist with which to evaluate the performance of the SVGL prototype tool. From this initial work the IBM/MIT Lincoln Labs 193 nm single layer positive tone resist, version 1.0 emerged. In 1993 sub-quarter micron imaging was demonstrated at 0.225 µm with the MS-193 tool utilizing the IBM/MIT-Lincoln Labs version 1.0 resist(13). The chemistry of this resist system was based on t-butyl acrylate polyacrylic materials and onium salt PAGs adapted from an earlier IBM printed circuit board resist application. The k1 factor for this demonstration was 0.58 and slightly larger than the k1 of 0.5 demonstrated for 248 DUV resists on 0.5 NA tools at the time. The version 1.0 resist was utilized extensively over the next year in the optimization of the optics of the prototype MS-193 system and greatly facilitated the timely completion of this system because of the significantly improved contamination resistance compared to 248 nm DUV resists reported at the same time. Thus, the laboratory demonstration of a useful 193 nm single layer resist was
accomplished a short 2 years after R&D on this class of materials was initiated. This very short time-lapse was indeed unusual in comparison with the period of time taken for the development of the first positive tone 248 nm DUV resist with similar performance characteristics. This short R&D feasibility cycle was enabled by utilization of principles learned from 248 nm resist development and efforts to improve both the contamination resistance and lithographic performance of 248 nm resist systems.

In the period since 1993 much has been learned by research teams working on 193 nm single layer resist systems. First, it became clear that the utilization of polyacrylic materials for 193 nm, necessitated by the need for an optically transparent resin, resulted in a photoresist with very poor reactive ion etch resistance. Second, it became clear that one of the common shortcomings of the polyacrylic resin systems was that the only convenient functionality that could be used to gain aqueous base solubility was methacrylic acid or acrylic acid and that this hydrophilic functionality with a pKa of 5 compared to 9 for the hydroxystyrene hydrophilic functionality of 248 nm DUV resists led to difficulties with strong base developer compatibility.Compatibility with aqueous base developers was further compounded by the introduction of hydrophobic cyclic aliphatic functionality into the resins to achieve RIE resistance.

The first examples of improvement in RIE etch resistance of a polyacrylic 193 nm resist was published Kaimoto(16) and Allen(15) with the utilization of an adamantane or adamantane-methyl methacrylic ester functionality to improve RIE etch resistance. This work was shortly followed by a number of publications on the introduction of pendent cyclic aliphatic functionality into 193 nm resist systems(17, 18) and the demonstration of promising progress toward realization of RIE etch resistance that approached novolac based resists. The approaches range from use of additional methacrylic ester functionality such as isobornyl methacrylates at IBM(15) to the mevalonic lactone by Nozaki(19) and the red shifted 2-naphthylmethacrylate work of Nakase(22). Most of this early work involved acrylic ester functionality that was passive to the deprotection chemistry required for imaging these materials.

4. 193 nm Imaging Chemistry

The first demonstration of 193 nm single layer resist lithography by IBM/MIT-Lincoln Labs utilized the t-butyl methacrylate, acid labile functionality. This functional group was chosen because it had proven to be a chemically and thermally stable protecting group that was utilized widely in 248 nm resists with excellent success and even today provides the imaging chemistry for one of the most high resolution and contamination resistant DUV resists commercially available. Later, variations on the high activation energy deprotection chemistry for generation of a carbonium ion were
introduced by Fujitsu (19) in the form of the 3-oxocyclohexyl methacrylate and mevalonic lactone methacrylate (20). Finally, a few groups of researchers combined acid deprotection lability with RIE resistance by introducing the isobornyl methacrylate function, IBM (21), and the t-methyl adamantyl methacrylate, termed MAdMA by Nozaki (22). A summary of the acid labile protection group chemistry utilized today in 193 nm positive tone DUV resists is shown in Figure 6.

Since 248 nm DUV resist chemistry utilized acetal and ketal protecting groups, it seemed useful to introduce similar chemistry into 193 nm resists. In Figure 1 is also depicted the most widely utilized low activation energy protecting groups tetrahydropyranyl and tetrahydrofuranyl. All of the protecting groups in Figure 1 produce imaging chemistry although some have been utilized in conjunction with a more reactive function.

![Figure 1. Acid Labile Functional Groups in 193 nm Resists](image)

5. Photoacid Generators

The development of 248 nm CA type resists has led a large assortment of photoacid generator chemistries reported in the literature all of which contain aromatic and highly 193 nm absorbing functionality. Hence, the search for photoacid generators began with the concern that the absorbance of 248 nm photoacid generators would be too high for 193 nm applications. This concern has led to two findings: First a number of highly efficient 193 nm photoacid generators are possible which do not contain aromatic functionality. Figure 2 contains a summary of the most widely reported photoacid generators for 193 nm resists.
The most extensive study of nonaromatic photoacid generators has been conducted by Nakano and coworkers(20). In this study a series of trialkylsulfonium and mixed alkyl, aryl sulfonium triflates were compared for 193 nm absorbance and efficiency of acid generation. The findings of these workers indicate that the efficiency of photoacid generation in this family of materials is not related to absorbance, to first order. It is reasonable to conclude that the photodecomposition of these materials could indeed be complex with numerous reaction channels.

The second finding on 193 nm photoacid generators is that many aromatic sulfonium and iodonium photoacid generators do indeed have a low enough absorbance to be useful in 193 nm applications. However, the utility of highly aromatic PAGs is dependent on the use of very low absorbance resins and relatively low level loading of the aromatic PAG in the resist formulation.

### 6. 193 nm Lithography

The lithographic performance of 193 nm single layer, positive tone resists formulated with the chemistry options described above has been reported by many research groups. However, because of the lack of availability of high NA 193 tools the actual availability of detailed 193 nm resist performance data is quite limited. For example, while many groups have published information on the feasibility of imaging sub-quarter micron features with resist chemistry under development there have actually been only two systems world-wide, until recently, on which feasibility imaging could be evaluated. These systems have been the 0.6 NA 193 MSII at MIT-
Lincoln Labs in the US and the 0.55 NA, 193 mini-stepper at NIKON Precision in Japan. Recently Integrated Systems incorporated (ISI) has developed a small field 193 nm mini-stepper, on which we have been able to image the IBM 193nm version 1B resist with outstanding success. Figure 3 depicts a normal incident SEM view of 0.15 µm images produced on this resist development tool and is a promising indication that both 193 nm tool optics for sub 0.18 µm resolution and DUV resist materials have reached a high level of feasibility.

Since so few 193 nm tools are available for photoresist R&D many groups have resorted to the use of high NA 248 nm tools for resist performance evaluations. It is not a given that 193 nm resists may be routinely evaluated at 248 nm because the photochemical mechanisms by which photoacid is generated at 248 nm often involve a large component of electron transfer sensitization from the hydroxystyrene resin of these systems. However, it has been our experience that PAGs that function effectively at 193 nm do most frequently function at 248 nm, albeit with much lower acid generation efficiency. However, the converse is not the general case, i.e. all 248 nm photoacid generators do not function effectively at 193 nm. Thus, demonstration of the feasibility of a 193 nm photoacid generator at 193 nm irradiation most often permits use of 248 nm lithography to evaluate the performance of a resist containing this PAG. One example of the comparison of 193 nm and 248 nm printing of a resist may be found in our efforts to compare lithographic performance of the IBM SLR, version 1B performance at 193 nm, shown in Figure 3, with results obtained at 248 nm. For this comparison we have patterned this resist on a NIKON, 248 nm, 0.6 NA tool. The results obtained indicate excellent resolution with vertical wall profiles in 0.25 µm l/s patterns with similar results for the images of 0.30 µm vias at the same dose. These results indicate that this first
generation 193 nm resist, when patterned at 248 nm exhibits lithographic performance similar to the first generation commercial 248 nm photoresists.

6. Commercialization of DUV Photoresists

The availability of photoresists and lithography manufacturing tools to the world-wide semiconductor community may be characterized as a "chicken and egg" series of events. For example, in the early 1990s when NA>0.50 I-Line tools were available but resists with potential for 0.35 µm manufacturing performance were not commercially available. In the same era, 248 nm, 0.5 NA DUV lithography tools were available but 248 nm DUV resists with adequate performance were not commercially available. (Note, these 248 nm DUV tools were first generation systems.) In this same period semiconductor companies were manufacturing products at 0.5 µm dimensions, semiconductor development was conducted at 0.35 µm dimensions but few, if any, semiconductor companies were manufacturing at 0.35 µm dimensions. As soon as serious 64 Mb DRAM product development began in the mid 1990s the question of whether I-Line or DUV lithography would be utilized for manufacture of this generation of DRAM arose. Out of this two wavelength choice emerged I-Line lithography as the dominant choice for 64 Mb DRAM manufacturing although it appears that 248 nm, 0.5 NA DUV lithography has become the choice for manufacture of Logic products. From this series of situations and events, it would be useful to develop an understanding of the paradigm by which new lithography tooling and photoresist products emerge for commercial use by semiconductor companies.

One approach to understanding the timing of new, commercial, lithography tool and resist availability is to consider the historical sales trends and market forecasts for these two products. Figure 4 contains plots of historical and predicted lithography tool sales for both I-Line and 248 nm DUV systems generated in 1995. At that time it was expected that nearly 1000 I-Line steppers and somewhat more than 50 248 nm DUV systems would be shipped in 1995. Both predictions appear to be fairly accurate. It is clear from Figure 4 that the growth of 248 nm DUV tool shipments has been very slow over the period of 1992-1995, the growth of I-Line tool shipments has been dramatic over the same period and that significant growth of 248 nm tool shipments is predicted beyond 1996. Dataquest has published information on total DUV manufacturing tools installed worldwide as well as the corresponding volume of 248 nm DUV resist expected to be sold for use of these tools. Figure 5 contains graphs of both these predictions from the present until the year 2002. This prediction indicates that the growth of installed DUV tool base and photoresist sales will be very significant over this period but that the volume of DUV resist sales will be relatively low until well after the year 2000.
7. Conclusions

The R&D of 193 nm DUV photoresists has progressed at an unusually rapid pace since the inception of this work in 1992. Many concepts have been adapted from 248 nm DUV resist chemistry and applied to 193 nm resists. In many ways the complexity and variety of new chemistry published in the past few years for 193 nm resists exceeds that published for 248 nm resists in the same period of time. Significant technical challenges exist in the effort to develop practical 193 nm photoresists suitable for single layer resist applications to semiconductor fabrication. One of these challenges is the introduction of RIE etch resistance into 193 nm resins and significant progress toward this end is being made by a number of research groups.

The commercialization of 248 nm DUV resists is still in the early stages of realization and has progressed much more slowly than expected. In a similar manner the consumption of 248 nm DUV resists by semiconductor manufacturers has advanced quite slowly. If the slow rate with which the semiconductor industry as adopted 248 nm phototresists is any guide, the commercialization of 193 nm DUV phototresists will not occur for many years.
8. References


397