Development of New Advanced Resist Materials for Microlithography

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This paper reviews development of advanced resist materials which I have been involved in for more than a quarter century. First, our attempts to increase the main chain scission susceptibility are described. Next, a simple lift-off process for fabrication of magnetoresistive heads for storage devices is presented, which became the industry-standard manufacturing technology. Then, the major focus is going to be placed on the development of chemical amplification resists. Chemical amplification resists achieve a high sensitivity through a catalytic action of a photochemically generated acid. This drastically novel imaging concept was considered laboratory curiosity initially. However, the very first chemically amplified tBOC resist was quickly implemented in mass production of 1 me gabit dynamic random access memory devices by deep UV lithography at IBM. Since then the chemical amplification concept has become the paradigm of advanced resist systems, enabling the industry to continue to migrate to shorter wavelengths (from 365 to 248, and then to 193 nm) for higher resolution and to follow the Moore's law. The chemical amplification resist invented for 1 μm resolution can now resolve <30 nm equal line/space patterns and continues to play a pivotal role in microlithography in the foreseeable future.

Keywords: poly(methyl 2-trifluoromethacrylate), poly(isopropenyl t-butyl ketone), polymethylglutarimide, chemical amplification, photochemical acid generators, acidcatalyzed deprotection, tBOC, APEX, ESCAP, fluoroalcohol

1. Introduction

We have witnessed an astonishing advancement of microelectronic devices in the last quarter century. The improvement of the performance of semiconductor devices at a remarkable rate has been accomplished by increasing the number of components through reduction of the minimum feature size on the chip. The rapid innovation cycles unique to the semiconductor technology have been often expressed by the famous "Moore's Law" and the cost per bit decreased ten thousand times from 1980 to 2000.

As the wafer throughput directly connects to the cost, the high resist sensitivity has always been an important requirement. Thus, in the late 70's and early 80's improvement of the main chain scission susceptibility of poly(methyl methacrylate)-type polymers for deep UV and electron beam lithography was a major research subject.

Photolithography employing ultraviolet (UV) irradiation has been the dominant technology for device manufacture for the last five decades, achieving a higher resolution by migrating to a shorter wavelength. However, each generation of a new technology required introduction of new resist materials.

Chemical amplification resists were proposed in the early 80's have enabled the lithographic technology to migrate to wavelengths below 300 nm and have become the foundation for the current and future device manufacturing.

2. Degradable Polymers

Poly(methyl methacrylate) (PMMA) was the first polymer to be used as a deep UV and electron-beam resist and is characterized with a high resolution capability. However, its sensitivity is unacceptably low. A wide range of PMMA analogs and copolymers were synthesized and evaluated in attempts to identify a polymer with the desirable processing properties of PMMA and
with sufficient sensitivity to be considered for use in production of photomasks or actual devices. 

Introduction of α-substituents with a strong inductive electron-withdrawing effect increases the scission efficiency ($G_v$) of the polymer. However, α-F substitution resulted in increase in crosslinking efficiency ($G_c$) due to HF elimination to form C=O double bonds in the backbone. We decided to incorporate strongly electron withdrawing CF$_3$ into the α-position, which would not eliminate F upon irradiation. However, methyl 2-trifluoromethylacrylate (MTFMA) did not undergo radical homopolymerization or anionic polymerization with butyllithium or a Grignard reagent which are typical initiators for MMA due to F elimination after β-addition. The highly electron-deficient MTFMA (Alfrey-Price ε=2.5) was successfully polymerized using unconventional anionic initiators such as pyridine, potassium acetate, potassium cyanide, potassium t-butoxide, etc. Poly(methyl 2-trifluoromethylacrylate) (PMTFMA) thus prepared was found to have a $G_v$ value of 2.6, twice more sensitive to γ-radiation than PMMA ($G_v$=1.3), with immeasurable $G_c$. Electron beam imaging results of the PMTFMA resist are presented in Figure 1. 2-Trifluoromethylacrylates were resurrected after twenty years as a 157 nm resist platform.

![Fig. 1 Scanning electron micrographs of positive images printed in PMTFMA by e-beam lithography](image)

Poly(vinyl ketones) are another class of photodegradable polymers, which undergo Norrish type-I or type-II photolysis. As the type-II pathway involving a cyclic intermediate is not favored in the solid state, we wanted to increase the propensity for the type-I cleavage (Fig. 2) and undertook polymerization of isopropenyl t-butyl ketone (IPTBK). However, we have found that the C=C and C=O double bonds of IPTBK are not coplanar and therefore not conjugated and that IPTBK does not undergo radical homopolymerization. $n$-Butyllithium (BuLi) and phenylmagnesium bromide failed to polymerize IPTBK, though vinyl ketones are reactive monomers in anionic polymerization as well as in radical polymerization. Based on our detailed investigation on the reactions between IPTBK and several anionic initiators, we selected t-BuLi for the polymerization of IPTBK, which added cleanly and rapidly to the β-carbon of IPTBK at 25 °C without contamination with propagation or addition to C≡O. IPTBK and t-BuLi were mixed in tetrahydrofuran at room temperature to promote clean and fast initiation and then cooled to -78 °C to promote propagation by shifting the equilibrium to the polymer side. While the quantum yield of main chain scission ($Q_d$) for poly(methyl isopropenyl ketone) (PMIPK) and PIPTBK is essentially the same in solution (0.45), the latter degrades >10 times more efficiently than the former in the solid state (0.024 vs. 0.29, Fig. 2). In addition to the more facile Norrish type-I cleavage, the steric hindrance, the lack of radical homopolymerizability, and the low ceiling temperature ($T_c$) contribute to the high chain scission efficiency.

![Fig. 2 Norrish type-I photolysis in PMIPK and PIPTBK](image)

3. Metal Lift-Off Process for Magneto-resistive Head Fabrication

A lift-off process utilizing an undercut resist pattern produced by image reversal of a diazonoaphthoquinone (DNQ)/novolac resist was attempted in fabrication of magnetoresistive heads for storage devices. However, sputtering to deposit metal on the substrate resulted in covering of the resist sidewall and in fence formation after lift-off and scrubbing. In order to facilitate ready and clean lift-off without fening, we employed a bilayer film stack consisting of a thin poly(methyl glutaramide) (PMGI) layer on the substrate and a DNQ/novolac resist. PMGI can be overcoated
with a photoresist without interfacial mixing.\textsuperscript{18} The bilayer stack was exposed to near UV radiation and developed with aqueous base. The development was continued without interruption to create a deep undercut by dissolving the PMGI layer. The metal sputtering, which is blizzard-like, could not get into the deep cave with a small opening (Fig. 3). Stripping solvent such as N-methylpyrrolidone (NMP) or aqueous base could flood the cave through the opening and dissolve the PMGI layer, facilitating facile clean lift-off.\textsuperscript{17} This simple lift-off process became a standard manufacturing technique of magnetoresistive heads in the entire storage industry.

to generate one useful product have inherently limited sensitivities.

4.1. Initial Demonstration of Chemical Amplification

We first chose depolymerization of polymers that are characterized with low T\textsubscript{c} as a mechanism to achieve a dramatic increase in sensitivity.\textsuperscript{1} We selected polyphthalaldehyde\textsuperscript{20} (Fig. 4) as a candidate, and polymerized phthalaldehyde anionically using break-seals under high vacuum, which provided clean end-capping for stability. Depolymerization was, however, only partial upon deep UV or γ-irradiation at room temperature.\textsuperscript{1} Incorporation of a classical photosensitive o-nitrobenzyl group resulted in only about 50% depolymerization.\textsuperscript{1} We had to change our strategy. Polyaldehydes are polyacetics like polysaccharides, which depolymerize even at cryogenic temperatures during cationic ring-opening polymerization of anhydrosugars with a Lewis acid generated by heating a diazonium salt.\textsuperscript{21} Diazonium salts are also sensitive to light. First I tried a couple of diazonium salts and quickly moved to onium salt cationic photoinitiators such as triphenylsulfonium and diphenylylodonium metal fluorides pioneered by Crivello\textsuperscript{22} for photochemical curing of epoxy resins. The polyphthalaldehyde film containing an onium salt depolymerized upon deep UV irradiation, producing relief images spontaneously without a subsequent solvent development process, which we coined “self-development” (Fig. 5).\textsuperscript{1}

4. Chemical Amplification Resists

Migration from near UV (∼400 nm) to mid UV (313 nm), and then to deep UV (254 nm) was sought in IBM in the late 1970’s. The shift from near to mid UV was rather easily achieved simply by modifying novolac-DNQ resists.\textsuperscript{19} However, migration further down to deep UV was much more challenging. The output of a Xe-Hg lamp in the deep UV region was so small, <30 times of near UV radiation, that a dramatic increase in resist sensitivity was required to achieve economically feasible wafer throughputs. Thus, it was clear that a gain mechanism in chemistry or processing was needed to meet the sensitivity requirement because the resist systems based on photochemical events that require several photons

\begin{align*}
\text{Fig. 3 Bilayer metal lift-off with PMGI for magnetoresistive head fabrication} & \\
\text{Fig. 4 Anionic polymerization and cido-catalyzed depolymerization of polyphthalaldehyde} & \\
\end{align*}
polymerization of cyclic ethers (anhydrosugars) using a thermally generated Lewis acid initiator and we were interested in direct photochemical crosslinking of the epoxy resin by using cationic photoinitiators instead of converting epoxy to methacrylate for radical crosslinking. Crivello was very active in photochemical curing of epoxy resins usingonium salt cationic photoinitiators. Exposing a SU-8 film (6 μm thick) containing a diazonium salt absorbing above 300 nm to 313 nm radiation produced high quality negative images with an aspect ratio of 1.5 (Fig. 7).1

We were interested in poly(4-hydroxy-α-methylstyrene) (Fig. 6),23 which was expected to be soluble in aqueous base and to undergo main chain scission upon irradiation. Cationic or anionic polymerization had to be carried out, with the hydroxyl group protected. tert-Butyloxycarbonyl (tBOC), most commonly employed in peptide synthesis, was one of the protecting groups selected. Anionic polymerization of α-methylstyrenes requires a strong initiator such as alkyllithium, which destroyed the tBOC group even at −78 °C.23 Cationic polymerization in CH₂Cl₂ with BF₃·OEt₂ or PF₅ at −78 °C resulted in significant cleavage of the acid labile tBOC group.23 Use of electrophilic liquid SO₂ as a solvent for cationic polymerization of tBOC-protected 4-hydroxy-α-methylstyrene with BF₃·OEt₂ successfully produced a polymer with the tBOC group intact (Fig. 6).23 When acid was generated in the tBOC polymer film, clean acid-catalyzed deprotection was demonstrated by IR spectroscopy using an onium salt acid generator (Fig. 7). The net result of the deprotection reaction was a conversion of a nonpolar polymer to a polar acidic polymer. Use of a polar solvent such as alcohol or aqueous base as a developer resulted in formation of positive tone images of the mask (Fig. 8). Conversely, organic solvents such as chloroform and dichloromethane produced negative images (Fig. 8). As it was not practical to prepare polymer by cationic polymerization in liquid SO₂, we decided to work with a styrene, 4-t-butoxy carbonyloxystyrene (BOCST), which had been polymerized by using a radical initiator.24

My third project was concerned about crosslinking of an epoxy resin, Epi-Rez SU-8 (Fig. 9). The epoxy rings of the resin were opened and converted to methacrylates for photochemically initiated radical crosslinking for a circuit board application in IBM at that time. The conversion of epoxide to methacrylate was irreproducible. I worked at SUNY on cationic ring-opening...
polyphthalaldehyde as a polymeric dissolution inhibitor of a novolac resin in the design of aqueous base developable positive resists to overcome the poor etch resistance of the depolymerizable polymer. During the course of this work, we discovered that certain onium salt photochemical acid generators (PAGs) are excellent dissolution inhibitors of novolac resins and function just like DNQ. Positive imaging is possible by aqueous base development of the two component non-amplified resist.

We did not pursue the crosslinking through cationic ring-opening polymerization any further but this system was followed up by our colleagues at IBM T. J. Watson Research Center and SU-8 has become the thick resist of choice for MEMS applications.

In 1980 we demonstrated three modes of photochemically induced acid mediated imaging; 1) positive-tone self-development through acid-catalyzed depolymerization of polyphthalaldehyde, 2) dual-tone imaging based on a polarity change through acid-catalyzed deprotection, and 3) negative-tone imaging by crosslinking through cationic polymerization. We have termed the gain mechanism “chemical amplification.” I continued to work on the polyphthalaldehyde system, moving from self-development to thermal development to avoid exposure tool contamination, and then to a thermally-developable bilayer resist based on poly(4-trimethylsilylphthalaldehyde) (PSPA, Fig. 11). In addition to a conventional hard-baked novolac resin, we utilized deep-UV-opaque poly(4-vinylbenzoic acid) (PVBA) without crosslinking as a transfer layer in the all dry bilayer scheme, which can be overcoated with the Si-containing polyphthalaldehyde resist without interfacial mixing and can be easily dissolved in N-methylpyrrolidone (NMP) or aqueous base, facilitating clean stripping. We also employed PSPA/PVBA after O₂ RIE

after CF₄ RIE

after stripping with MF312

My patent disclosure on the dual tone resists based on acid-catalyzed deprotection was rated not to file initially but to be published in IBM Technical Disclosure Bulletin because this invention was considered simply an interesting laboratory curiosity and impractical. I kept generating higher quality images, appealed, and finally succeeded in filing a patent application on the dual tone resists including tBOC, which has become the foundation for the entire advanced resist systems. IBM quickly decided to implement the tBOC resist in 1 Mbit DRAM manufacture by deep UV lithography.

4.2. Advancement of Chemical Amplification Resists

The technology transfer was not smooth-sailing because the tBOC resist was not an
evolutionary but revolutionary new resist. However, IBM succeeded in manufacturing by deep UV lithography millions of 1 Mbit DRAMs having a minimum feature size of 1 μm, employing the negative-tone tBOC resist formulated with triphenylsulfonium hexafluoroantimonate and using anisole as a developer (Fig. 12). Near UV lithography with the novolac/DNQ resist was a dominant technology in the rest of the industry at that time.

Resist engineers and lithographers were initially skeptical about the resolution capability of chemical amplification. However, the concept, especially the deprotection mechanism for a polarity change, has spread quickly in the resist and lithography community. The explosion of research activities on the deprotection resists stemmed from the fact that this was the only viable option available for the design of aqueous base developable positive resists to replace the novolac-DNQ resist for deep UV lithography (employing KrF excimer lasers at 248 nm). The advent of excimer laser lithography did not curb the widespread interest in chemical amplification because the laser beam intensity was very much reduced on the wafer plane after passing through many optical elements such as etalon. The high resolution capability of chemical amplification helped its rapid and wide acceptance. Without a high resolution potential, chemical amplification resists would have been discarded quickly.

A number of base soluble polymers protected with tBOC were reported from several laboratories (first generation). Realization in IBM Microelectronics Division in NY that only partial protection was required to render the polymer insoluble in aqueous base gave rise to development of the APEX resist, which was the first general-use positive resist later made available along with the tBOC resist to all the chip makers. The second generation resists [partially protected polyhydroxystyrene (PHOST)] provided better adhesion and superior positive tone development with aqueous base.

The use of acid as a catalyst provides design versatility. Many new resist systems based on a variety of acid-catalyzed reactions have been reported, expanding the library of chemical amplification resists.

We studied esters with different activation energies of deprotection, employing benzyl, α-methylbenzyl, and α,α-dimethylbenzyl methacrylate polymers. Replacement of the phenyl group of the α,α-dimethylbenzyl ester with a cyclopropyl ring reduces the activation energy even further but the primary cation is generated through opening of the cyclopropyl ring, which reacts back with carboxylic acid (Fig. 13). The rearrangement is predominant in the presence of acid (66%) while thermolysis converts the ester to acid more cleanly.

![Fig. 12 Negative-tone tBOC resist images printed on topography using PE500 in the deep UV mode for 1 MBit DRAM Manufacture](image)

![Fig. 13 Acid-catalyzed rearrangement of cyclopropyl dimethylcarbinol ester](image)

Acid-catalyzed deprotection (deesterification) was combined with depolymerization by synthesizing poly(α-acetoxy styrene) (Fig. 14), which is similar in structure to the aforementioned poly(α,α-dimethylbenzyl methacrylate) and is characterized with a low T_{c} of 47 °C. Acidolysis generates a carbocation in the backbone, releasing acetic acid, which results in depolymerization and β-proton elimination to form polyphenylacetylene. In a similar fashion PBOCST was rearranged to place a quaternary carbon in the backbone through cyclization to form poly(4-methylene-4H-1,3-benzodioxin-2-one). This polymer loses only one mole of gas (CO_{2}) upon acidolysis and is converted to poly(α-hydroxyphenylacetylene).

Another polymer which undergoes acid-catalyzed depolymerization we worked on was poly(4-hydroxy-α-methylstyrene) prepared by
thermolysis of a tBOC-protected polymer which in turn had been synthesized by cationic polymerization in liquid SO$_2$.$^{23}$ A tertiary benzylic carbon cation generated by reaction of acid with tertiary ether, tertiary alcohol, or C=C introduced into the polymer end through intentional termination with alcohol, accidental termination with water, or termination by proton elimination, respectively, becomes the starting point of depolymerization.$^{39}$

![Acid-catalyzed deesterification followed by depolymerization](image)

Fig. 14 Acid-catalyzed deesterification followed by depolymerization

We extensively developed negative resist systems that do not involve crosslinking. The first example of such resist systems was the tBOC resist. The polarity change from a nonpolar to a polar state induced by acid-catalyzed deprotection of the tBOC resist allows negative imaging with a nonpolar organic solvent (Fig. 7). We have extended the concept to a reverse polarity change from a polar to a nonpolar state in the design of negative systems which can be developed with a polar solvent such as alcohol or aqueous base.$^{40-42}$ The chemistries we employed to induce the reverse polarity change were acid-catalyzed intramolecular dehydration (Fig. 15) and pinacol rearrangement (Fig. 16).

Intramolecular dehydration of pendant tertiary alcohol converts a hydrophilic functionality to a lipophilic olefin, providing negative images with alcohol as a developer. Similarly, the pinacol rearrangement, which involves acid-catalyzed dehydration of vic-diol, results in transformation of polar alcohol to less polar ketone or aldehyde (Fig. 16), providing a negative system that can be developed with alcohol. Aqueous base development has been achieved by synthesizing HOST copolymers containing pendant vic-diol (Fig. 17)$^{42}$ and also by blending a small vic-diol with a phenolic matrix resin.$^{40}$ The latter system functions on the basis of conversion of hydrophilic alcohol to dissolution inhibiting ketone, which hydrogen-bonds with phenol, through pinacol rearrangement.

![Acid-catalyzed intramolecular dehydration for a reverse polarity change](image)

Fig. 15 Acid-catalyzed intramolecular dehydration for a reverse polarity change

![Acid-catalyzed pinacol rearrangement for a reverse polarity change](image)

Fig. 16 Acid-catalyzed pinacol rearrangement for a reverse polarity change

![Aqueous-base developable negative resist based on pinacol rearrangement](image)

Fig. 17 Aqueous-base developable negative resist based on pinacol rearrangement
The deprotection chemistry has been successfully utilized also in the design of resists that can be developed with oxygen plasma without use of a developer solvent.\textsuperscript{43,44} The polarity change induced by deprotection is equivalent to a reactivity change, allowing selective silylation of the polar polymers such as PHOST, PVBA, or poly(methacrylic acid) produced in the exposed areas. O\textsubscript{2} RIE removes the organic polymer in the unexposed areas while the silicon polymer remains unetched, resulting in a negative tone imaging (Fig. 18).

![Image](image_url)

**Fig. 18** O\textsubscript{2} RIE dry development of the tBOC resist through selective silylation based on reactivity differentiation

### 4.3. Development of Positive Chemical Amplification Resist

While massive efforts were being directed toward development of deep UV positive resists based on the deprotection chemistry throughout the industry, a devastating problem surfaced; formation of a skin or T-top in images developed with aqueous base (Fig. 19). This insoluble surface layer in fact prevented IBM from using the positive tone tBOC resist in manufacturing. It was truly a serious problem, which threatened the future of the chemical amplification concept. We were puzzled for a long time why and how the surface insoluble layer was formed.

My colleagues have found that a trace amount on the order of <10 ppb of airborne basic substances absorbed in the resist film upon standing after exposure neutralizes photochemically generated acid and suppresses the deprotection chemistry in the surface layer.\textsuperscript{45} Amines in paints and in floor cleaning liquids and clean room chemicals as well as ammonia from human bodies cause the postexposure delay problem.\textsuperscript{45} They demonstrated that coated wafers stored in an air purified by activated carbon filtration were devoid of the contamination problem (Fig. 20).\textsuperscript{45} The activated carbon filtration of the wafer-enclosing atmosphere enabled IBM to implement the negative tBOC resist in manufacture of 1 Mbit DRAM\textsuperscript{42} and has become a common practice in the semiconductor industry.

![Image](image_url)

**Fig. 19** Skin and T-top formation in chemically amplified positive resist in aqueous base development

![Image](image_url)

**Fig. 20** Effect of activated carbon air filtration on image profile

Other engineering techniques proposed to ameliorate the airborne contamination problem included application of a protective overcoat to seal off contaminants and incorporation of a stabilizing base additive in resist formulation. The base additive for contamination resistance has been found to improve the resolution capability of chemical amplification resists by converting the sinusoidal curve of acid concentration in film more or less to a step function and by controlling acid
diffusion. Thus, all the advanced chemical amplification resist formulations contain a small amount of base, sometimes called a quencher, to enhance resolution.

The propensity of polymer films to absorb NMP was investigated by using a $^{14}$C labeling technique (Fig. 20). The concentration of $^{14}$C-labeled NMP absorbed in polymer films was measured. The first set of data was convincing enough to conclude that polymers with lower glass transition transition temperatures ($T_g$) absorb less NMP when baked at a given temperature (100 °C) due to smaller free volumes (better annealing) (Fig. 21). To confirm the validity of the annealing theory we prepared tBOC resists employing para and meta isomers and demonstrated that the lower $T_g$ meta version was more robust when baked at 100 °C, above its $T_g$ (Table 1).

![Fig. 21 NMP uptake in polymer films as a function of $T_g$](image)

**Table 1** $T_g$, residual PGMEA concentration and NMP uptake in para- and meta-PBOCSTs baked at 100 °C

<table>
<thead>
<tr>
<th>isomer</th>
<th>Mw/Mn</th>
<th>$T_g$ (°C)</th>
<th>residual PGMEA (wt%)</th>
<th>NMP uptake (ng/wafer)</th>
</tr>
</thead>
<tbody>
<tr>
<td>para</td>
<td>92,700/56,600</td>
<td>130</td>
<td>0.60</td>
<td>931</td>
</tr>
<tr>
<td>meta</td>
<td>57,200/34,400</td>
<td>85</td>
<td>0.55</td>
<td>99</td>
</tr>
</tbody>
</table>

However, as low $T_g$ resists suffer from thermal flow during device fabrication processes involving a significant temperature excursion, we designed a high $T_g$ resist that could be baked at a relatively high temperature (~150 °C), higher or close to $T_g$ of resist polymer. Chemical amplification positive resist polymers are hydroxystyrene copolymers and have relatively high $T_g$ (>2150 °C) and acid-labile protecting groups tend to be cleaved at a relatively low temperature (~130 °C) in the presence of acidic phenolic groups. A copolymer of HOST and t-butyl acrylate (TBA) (Fig. 22) was selected as a resist polymer along with a thermally stable acid generator which generated a bulky sulfonic acid. This resist film absorbed much less NMP when baked at an elevated temperature and demonstrated superb imaging that was barely affected by a long delay between exposure and bake. The resist was named "ESCAP (Environmentally Stable Chemical Amplification Positive resist)," which has become the industry standard 248 nm resist.

![Fig. 22 ESCAP 248 nm positive resist](image)

The tBOC deprotection chemistry was believed to be clean, releasing quantitative amounts of isobutene and carbon dioxide. However, quantitative $^{13}$C NMR analyses of exposed tBOC, APEX, and ESCAP films have revealed that the t-butyl cation reacts with the electron-rich phenolic group through O- and C-alkylation before it undergoes β-proton elimination (Fig. 23). The inverse-gated $^{13}$C NMR technique has proven useful also in quantifying residual casting solvents, such as PGMEA, ethyl lactate, and cyclohexanone, in postapply-baked resist films and in analyzing PAG photolysis in resist film.

![Fig. 23 Side reactions in acid-catalyzed tBOC deprotection](image)
The CN group of 2,2′-azobis(isobutyronitrile) (AIBN) used in radical polymerization is attached to the polymer end, which has been found to reduce the sensitivity of chemical amplification resists especially when the polymer molecular weight is low.51

4.4. 193 nm and Fluoroalcohol Chemical Amplification Resists

The microelectronics industry chose 193 nm lithography to extend the resolution to below 100 nm. New polymeric materials were required for this shorter wavelength technology as the 248 nm polymers consisting of HOST are too absorbing at 193 nm while the chemical amplification was the imaging mechanism of choice. Polymethacrylate-based chemical amplification resists were shown to be transparent at 193 nm (ArF excimer laser) by a MIT/IBM team.52 Aliphatic polymers, however, decompose rapidly during dry etching of substrates. A breakthrough was reported by Fujitsu researchers that alicyclic polymers are as resistant as phenolic resins toward plasmas.53 Thus, one class of 193 nm resists is based on polymethacrylates with pendant alicyclic groups such as adamantane (Fig. 24).

![Figure 24 Polymethacrylate 193 nm resists](image)

IBM initially promoted all-norbornene (NB) polymers containing the alicyclic structure in the backbone (Fig. 25) that were prepared by addition polymerization in collaboration with Promerus LLC (formerly BF Goodrich).54 The rigid backbone structure bearing pendant carboxylic acid exhibited tremendous swelling in aqueous base.55 For example, a copolymer of norbornene i-butyl ester and norbornene carboxylic acid does not dissolve when the ratio is 80/20 and dissolves rapidly at >20,000 A/sec in 0.26 N tetramethylammonium hydroxide aqueous solution when the composition is 40/60. The compositions between these two boundaries exhibit tremendous swelling that cannot be measured by our quartz crystal microbalance. By optimizing compositions and process conditions and by adding a dissolution modifying agent, high performance resists were developed.56 However, the swelling problem persisted.

![Figure 25 All-norbornane 193 nm resists](image)

The third class of the 193 nm resist platform was built by radical co- or terpolymerization of norbornenes with maleic anhydride (MA). We have found that this radical copolymerization does not involve a charge transfer complex and that methacrylate is consumed rapidly in the early stage of terpolymerization while acrylate is uniformly incorporated in terpolymer.57 We have also discovered that the anhydride ring opens during aqueous base development, boosting the contrast and dissolution rate in the exposed area.58 However, the matrix must be nonpolar in order to keep the anhydride ring intact during storage.58

Device production by 193 nm lithography has begun and efforts to further improve 193 nm resists to achieve <50 nm resolution are under way. Immersion lithography at 193 nm by placing water between the last lens element and resist film to effectively reduce the wavelength and to employ a hyper NA lens is being aggressively pursued to further increase the resolution to below 50 nm.

In 248 nm resists, the phenolic structure provides two functions in addition to transparency; dry etch resistance and base solubility. In 193 nm resists, alicyclic structures offer etch durability and carboxylic acid provides base solubility in many cases. Unfortunately, however, carboxylic acid polymers tend to swell in aqueous base developer, limiting resolution. We introduced hexafluoroisopropanol pendant from norbornene to
the design of new 193 nm resist polymers. Hexafluoroalcohol (HFA) is transparent at 193 nm and has a pKa similar to that of phenol (Fig. 26). Although TFMA monomers do not undergo radical homopolymerization, we have found that they can copolymerize by radical initiation with norbornenes and vinyl ethers according to a penultimate model (Fig. 29).

Fig. 26 Dissolution kinetics curve of poly(norbornene hexafluoroalcohol-alt-SO₂) in MF321

The HFA group has been shown later to be transparent enough at 157 nm (F₂ excimer lasers) and it has thus become the acid group of choice for the design of 157 nm resist polymers. The attractive dissolution behavior of the HFA group prompted us to replace the carboxylic acid with fluoroalcohol first in the all-norbornene system (Fig. 25), which resulted in much improved performance. Furthermore, the HFA group has been incorporated in our second generation methacrylate resists (Fig. 27) for dry and wet 193 nm lithography as well as in water and oil immersion topcoats (Fig. 28) and topcoat-free resists based on controlled segregation. Thus, although 157 nm lithography has been abandoned, HFA is a dominant player in our 193 nm resist design.

Fig. 27 HFA-bearing methacrylates for 193 nm resists

Interferometric immersion lithography employing a high refractive index and fluid successfully printed 30 nm line/space patterns in a JSR resist.

Another building block that we proposed for use in 157 nm resists and is still currently employed in 193 nm resists in the form of a topcoat is 2-trifluoromethylacrylate (TFMA) (2). Interests features of 193 nm methacrylate resists are common use of methylcyclopentyl, ethylcycropentyl, or methyladamanlantyl (MAd) protecting groups, which have a lower activation energy of deprotection than the t-butyl group, and heavy use of lactone to provide a polarity to hydrophobic alicyclic polymethacrylates. An even more reactive protecting group, ethylcyclooctyl, has been recently reported. Such bulky leaving groups tend to remain in resist film even after high temperature postexposure bake especially in the presence of a five-membered lactone (norbornane lactone methacrylate, NLM), which is much more basic than esters, carbonates, or large lactones. The deprotection fragment from the methyladamanlantyl methacrylate (MAdMA) remaining in the resist film after PEB reduces the
maximum dissolution rate in highly exposed regions (Fig. 30) whereas the ethylclooctyl methacrylate or t-butyl methacrylate (TBMA) does not suffer from such dissolution retardation.\(^{69}\)

![Graph showing dissolution kinetics curves of MA/MA/NLM and TBMA/NLM resists exposed to 46 ml/cm\(^2\) of 254 nm radiation and postbaked at 120 °C.](image)

**Fig. 30** Dissolution kinetics curves of MA/MA/NLM and TBMA/NLM resists exposed to 46 ml/cm\(^2\) of 254 nm radiation and postbaked at 120 °C.

4.5. Current Status of Chemical Amplification Resists

Finally, non-photo technologies such as extreme UV (EUV, 13.4 nm) and projection electron beam are also considered as next generation lithographic technologies for resolution below 50 nm. All these high resolution technologies demand high resist sensitivity for wafer throughput and therefore require chemical amplification resists. However, we may be approaching the resolution limit of chemical amplification resists due to acid diffusion (image blur) or even the resolution limit of polymeric resists. Electron-beam lithography with the IBM KRSS resist based on ketal produced 20 nm line/space patterns with some line collapse\(^{71}\) and EUV lithography successfully printed 25 nm line/space patterns.\(^{72}\) The chemical amplification resist invented for 1 μm resolution can now print 40-50 times smaller features. A difficult challenge that chemical amplification resists face currently is how to combine high sensitivity, high resolution and low line edge roughness (LER). Although a significant progress has been made, the EUV output is still very small, demanding even higher resist sensitivity, which could bring out a shot noise problem also.

In an attempt to increase resolution and to decrease LER, molecular glass resists\(^{73,74}\) smaller in size than conventional polymeric resists have been actively developed, showing some promise.

Can we achieve a satisfactory sensitivity without incorporating an amplification mechanism? No potential solution has been presented. More efforts to extend the limit of chemical amplification resists down below 50 nm resolution will have to continue.

5. Alternative Technologies

Nanoimprint has emerged as a promising and economical alternative technology for device manufacturing while the conventional photolithographic technology faces many critical challenges including the afore-mentioned sensitivity-resolution-LER trade-off of chemical amplification resists and almost formidable prices of exposure tools. Among several imprint schemes the step-and-flash nanoimprint technology invented by Willson\(^{88}\) and developed by Molecular Imprints is perhaps most suited for semiconductor fabrication.

The current step-and-flash nanoimprint lithography is based on photochemically induced radical polymerization of multifunctional acrylates.\(^{89}\) Because of its sensitivity toward oxygen (air), cationic photocrosslinking of vinyl ethers has been reported.\(^{90}\) We are interested in cationic crosslinking to design our imprint materials, which stems in part from our extensive experience with chemical amplification resists based on acid-catalyzed reactions. Therefore, we consider nanoimprint as an extension of the chemical amplification concept but not as a departure from it. In this respect, one of the three original chemical amplification systems included crosslinking of a SU-8 epoxy resin through cationic ring-opening polymerization of pendant epoxides. Epoxides have been employed in imprint recently.\(^{91}\) However, cationic ring-opening polymerization of epoxides is not fast and it requires cationic initiators with strongly non-nucleophilic gegen anions such as hexafluoroorontiminate,\(^{92}\) which are not accepted in current production environments. A much faster cationic polymerization of vinyl ethers with perfluoroalkanesulfonic acid as initiator (instead of metal containing superacids) was the major reason for our selection of vinyl ethers for imprint (Fig. 31).\(^{92}\) Vinyl ethers for step-and-flash nanoimprint lithography must have low viscosity and low volatility.

Low viscosity and low volatility vinyl ethers tend to be highly hydrophobic and selection of PAG is an important issue in designing vinyl ether imprint systems. In the case of the ionic PAG, diphenyltolylsulphonium triflate (DPTSOT) has a
good solubility in organic vinyl ethers such as diethylene glycol divinyl ether.\(^2\) Non-ionic CGI series PAGs (CGI261, 1905, 1906, and 1907) developed for ArF resists by Ciba Specialty Chemicals\(^3\) have been found to be highly soluble in our vinyl ether formulations (Fig. 32).\(^2\) We are interested in utilizing fluorinated vinyl ether as it could segregate to the surface, facilitating template release. Aromatic vinyl ethers are intended to be used in reverse-tone step-and-flash nanoimprint.

Upon mixing and an explosive reaction takes place when vinyl ether is present in the mixture.\(^2\)

A short shelf life of the vinyl ether formulations was a serious issue. Our sensitizers, anthMeOH and phenothiazine, can also function as a stabilizer (Fig. 32).\(^2\) While the vinyl ether formulation without a stabilizing additive solidified in less than two months, within 20 days in some cases, addition of a small amount of anthMeOH to the CGI or DPTSOt formulation and of phenothiazine to DPTSOt formulation greatly improves the shelf life to at least several months, one year, or even two years at room temperature.\(^2\)

We look at the imprint technology as a system, paying our attention to every layer, adhesion, release, etc. We are interested in employing the easily strippable PVBA as a transfer layer and O-(vinloxybutyl)-H-(triethoxysilylpropyl)-urethane (Gelset) as an adhesion layer between the transfer layer and the vinyl ether etch barrier layer. The triethoxysilyl moiety reacts with the carboxylic acid (or OH) of the transfer layer and thus covalently links the vinyl ether group of the adhesion promoter with the transfer layer. The vinyl ether group bonded to the transfer layer mixes with vinyl ether of a dispersed etch barrier material and undergoes cationic polymerization. Thus, the etch barrier layer is covalently bonded with the transfer layer through the adhesion layer.

Preliminary imprint experiments produced 50 nm dense line/space patterns on a Molecular Imprints Imprio 55 (Fig. 33).\(^2\)

While CGI1905, 1906, and 1907 are sensitive to i-line irradiation due to their small absorptions in the 365 nm region, the CGI261 sensitivity is extended to only mid UV (313 nm) radiation. We have found 9-anthracenemethanol (anthMeOH) to be a good i-line sensitizer of DPTSOtI and CGI261 (and also CGI1905-1907) (Fig. 32).\(^2\) Furthermore, phenothiazine has been found to efficiently sensitize DPTSOtI to i-line (Fig. 32). However, phenothiazine reacts with the CGI PAGs
encouragement. His gratitude goes also to his IBM colleagues, alliance partners, collaborators, visiting scientists, postdoctoral associates, and students for their valuable contributions to the works described in this paper.

References


