

Review

Chemistry of photolithographic imaging materials based on the chemical amplification concept

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Received 18 September 2007; received in revised form 14 December 2007; accepted 21 December 2007

Available online 12 January 2008

Abstract

This review describes the versatile chemistry of photolithographic imaging materials developed for nanofabrication of semiconductor devices. Conventional photoresists based on novolac/diazonaphthoquinone systems are not appropriate for the generation of relief images under sub-100 nm. In order to employ deep UV radiation techniques that are required for nanopattern generation, such as with 248, 193 and 157 nm excimer lasers, completely different strategies are required. Incorporation of chemical amplification concept into the design of resist systems has led to significant breakthroughs in the photolithography industry. In a chemically amplified resist system, a cascade of chemical events is promoted by photochemically generated initiating molecules. This leads to changes in the chemical or physical properties of the resist systems which typically develop during the postexposure baking procedure. Polarity change of the resist polymer along with depolymerization and crosslinking strategies has been widely employed in chemically amplified systems. Chemistry related to radiation resists using high-energy photons and charged particles, such as extreme-UV, X-ray, electron beam, ion beam has also been developed.

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Keywords: Photolithography; Chemical amplification; Photoacid generator; Photoresist

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1. Introduction

The development of efficient methods for the fabrication of sub-100 nm relief images on solid substrates has been the central focus in the electronics industry. Surface probe lithography technologies employing atomic force microscopy (AFM) or an approach using self-organization and self-assembly can be utilized for nanopatterning. However, nanolithography based on light irradiation has proven to be the most reliable method for the fabrication of integrated circuit (IC) and large-scale integration (LSI) device from mass production and economic points of view.

The circuit element density of semiconductor LSI has rapidly been increased, roughly quadrupling every 3 years. Currently, lithography technologies capable of resolving sub-80 nm features are being commercialized. Such a rapid shrinkage in circuit densities has been achieved mainly by improving resolutions of photoresist and light-exposure tool.

Photoresists are photosensitive protective films on substrates that have etching resistance. In order to fabricate LSI devices, silicon wafers are coated with solutions of photosensitive materials to give 0.5–1.0 μm -thick films. The photosensitive films are prebaked, irradiated with UV light through a photomask, and postbaked. The photoinduced chemical reactions that occur in the exposed areas alter the physical or chemical properties of the resist materials in the exposed areas. The resulting property change produces differences in dissolution rates in a subsequent

image development step. Consequently, selective dissolution of either the exposed or the unexposed areas of the resist film affords positive or negative mode relief images (Fig. 1).

From the standpoint of wave optics, resolution can be improved by using shorter wavelength light sources (see Table 1) [1–3]. The emission spectrum of high-pressure mercury arc lamps contains strong peaks at 436 and 365 nm, and a weak peak at 254 nm. Although associated with the highest resolution, the 254 nm peak from high-pressure mercury arc lamps is weak, necessitating the use of resists that have high sensitivity (chemically amplified photoresists) as well as light sources with high emission intensity (excimer lasers) [4–6].

Diazonaphthoquinone (DNQ) derivatives were synthesized by Oskar S. (a chemist in the Kalle Company) around 1940 and the first DNQ/novolac system was introduced in a positive-tone printing plate around 1950 [7]. Since then, DNQ-based photoresists have been so widely used as g- or i-line resists in the manufacture of microelectronic devices. The DNQ-based resists show high resist contrasts, excellent etch resistance and no swelling in an aqueous base developer. Unfortunately, these resists have high absorption and low sensitivity to deep UV light even when processed by using excimer lasers, due to high absorption of both novolac binders and DNQ used in relatively large amounts. As a result, the design of new resist materials, which are highly transparent (*i.e.*, low absorptivity) and photochemically sensitive even in a small amount to deep UV light, is required.

High sensitivity and resolution can be incorporated into photoresists by exploiting the chemical amplification concept. Chemical amplification means that the photochemical processes that induce changes have effective quantum efficiencies that are higher than one. A typical example of a chemical amplification reaction in resist systems is acid-catalyzed reactions promoted by Brønsted or Lewis acids photogenerated from photoacid

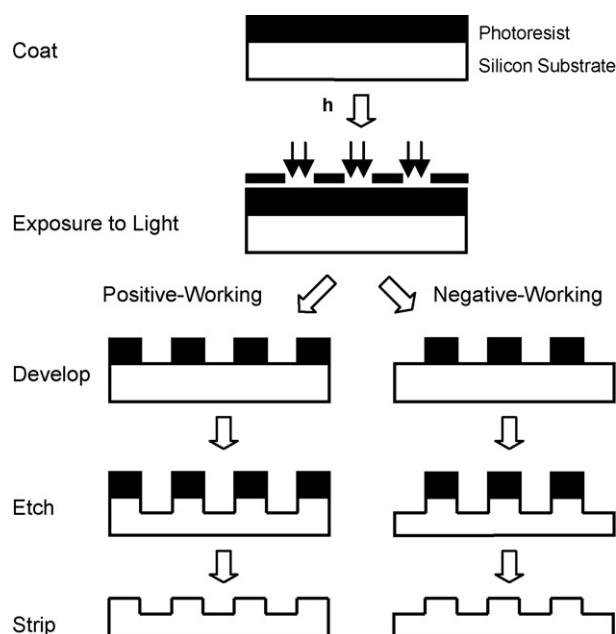


Fig. 1. General nanolithographic process.

Table 1

Resolution improvement according to reduction of the incident light wavelength for different lithography technology generations

Year	Feature size (nm)	Incident light (λ , nm)	Chemistry	Light source
Till 1988	1200–800	436 (g-line)	Diaz-naphtho-quinone-based photoresist	High-pressure mercury arc lamp
1988–1995	800–350	365 (i-line)		
1995–2003	350–90	248	Chemically amplified photoresist	KrF excimer laser
Since 2003	90–60	193		ArF excimer laser

generators (PAG). In such systems, the primary photochemical event is dissociation of PAG as a cationic photoinitiator. A single molecule of photogenerated acid then serves to initiate a cascade of bond-making or breaking reactions. Thus, the effective quantum efficiency of the overall process is the product of the photolysis reaction efficiency times the catalytic chain length. Because of this, the initial photochemical event induced by absorption of a photon is amplified to induce multiple reactions. Chain polymerization and depolymerization by unzipping process are also other examples of chemical amplification.

Below, we describe the versatile chemistry of imaging systems from conventional DNQ-based photoresists to next

generation radiation resists, with an emphasis on chemical amplification. This report also includes currently commercially available many resists and their resist chemistry. Although some other reviews concerning chemical amplification resists exist [8,9], we believe that our report provides useful information about the design of new resist chemistry and resist systems.

2. Conventional DNQ-based photoresists

Semiconductor devices using g- or i-line light from a high-pressure mercury arc lamp as the light source have been

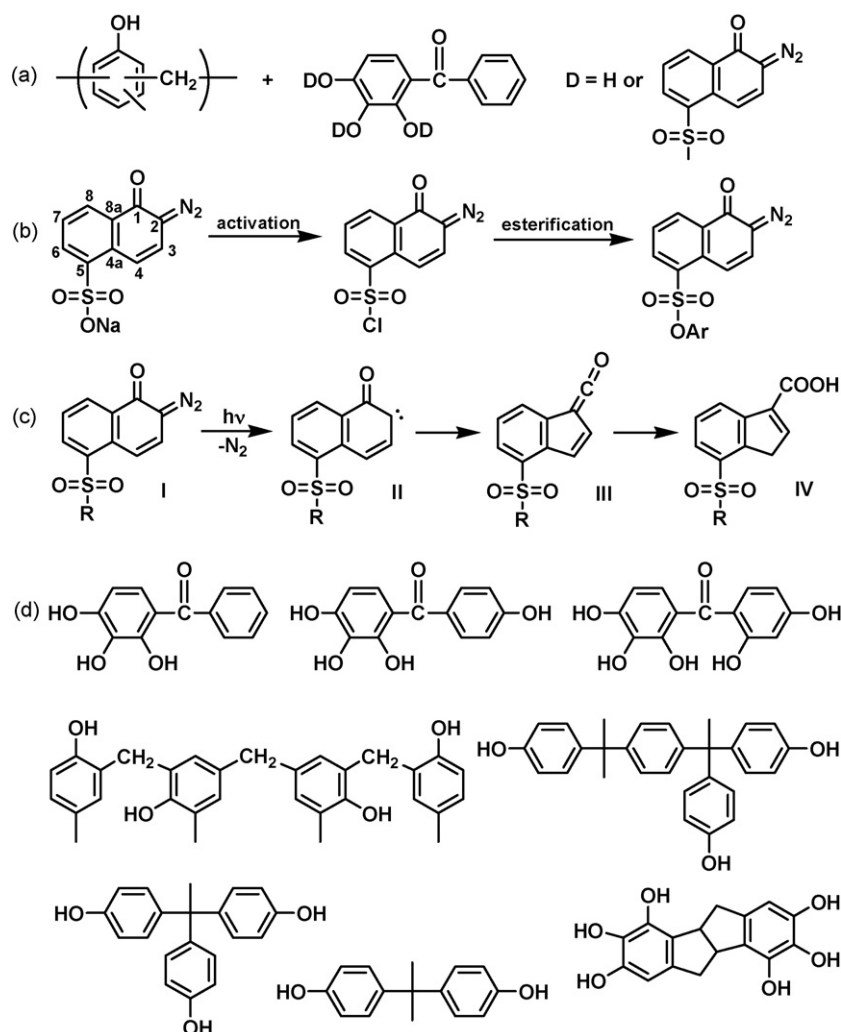


Fig. 2. DNQ-based positive-working photoresists. (a) General composition, (b) synthesis of DNQ-5-sulfonates, (c) photolysis of DNQ-5-sulfonates, and (d) typical ballast structures.

manufactured by using a photoresist composed of DNQ derivatives and a novolac resin as shown in Fig. 2(a) [7,10–24].

A typical novolac resin is a condensation polymerization product of formaldehyde with a mixture of *m*- and *p*-cresol isomers formed under acid-catalyzed conditions. In addition, a variety of phenolic compounds, such as phenol or pyrogallol, and ketones such as acetone, can be used to form these types of resins. The molecular weight of novolacs is not very high. The number average molecular weight, M_n , usually lies between 1000–3000 and the weight average molecular weight, M_w , is nearly 20,000 as determined by using gel permeation chromatography (GPC) with polystyrene standards [7,10–12].

DNQ derivatives are known to exist in the 4-, 5- or 6-form according to the position of sulfonate groups, but the 5-form is used overwhelmingly. As shown in Fig. 2(b), DNQ derivatives are synthesized by reacting 2-diazo-1-naphthol-5-sulfonylchloride (NAC) with the ballast group in Fig. 2(d) under base-catalyzed conditions. NAC is obtained by reacting 2-diazo-1-naphthol-5-sulfonic acid sodium salt monohydrate (NAS) in the presence of thionyl chloride and chlorosulfonic acid, since NAC does not have sufficient thermal stability to be commercially available [7,13–15].

Photoactive DNQ derivatives are hydrophobic and act as a dissolution inhibitor through physical or chemical interactions with novolac to give insolubilized novolac/DNQ films in aqueous base developers. When DNQ-5-sulfonate derivatives are irradiated with UV light, the hydrophobic DNQ in the exposed areas undergoes either a concerted or 2 step (through an intermediate ketocarbene species II) Wolff rearrangement reaction to form the indenylidene ketene III. The unstable ketene III undergoes either 1,2-addition of water followed by a rearrangement of the resulting 1-indenecarboxylic to 3-indenecarboxylic acid or a direct 1,4-addition of water to afford the indene-3-carboxylic acid IV. As a result of this chemistry, exposed areas are rendered soluble in the developer, thereby, allowing the system to exhibit positive behaviour [7,16–22].

Bleaching is highly important for the performance of the resist. With increasing exposure to irradiation, absorption due to the DNQ chromophores is bleached, while that due to ballast

groups remains unchanged. Therefore, careful selection of ballasts is required so that they are transparent in the wavelength region of the irradiation light. Examples of typical DNQ ballasts are given in Fig. 2(d) [7,20–24].

3. Chemically amplified photoresists

3.1. Photoacid generators (PAG)

As mentioned above, the employment of deep UV light for formation of imaging patterns requires chemically amplified photoresists with high sensitivity. Chemical amplification is accomplished by employing PAGs which produce strong acids upon irradiation that promote catalytic or chain reaction.

The first chemically amplified photoresists were based on the cationic polymerization of epoxy resins. Schlesinger synthesized a number of aryldiazonium salts, carried out the acid-initiated ring-opening polymerization of epoxy resin films, and obtained negative-working images in an organic solvent developer [25,26]. Aryldiazonium salts produce Lewis acids on irradiation as shown in Fig. 3(a) and their spectral sensitivity is extended from the deep UV region to the visible region by varying the type of aromatic groups incorporated into the structures. However, the aryldiazonium salt are thermally unstable and they produce nitrogen gas upon irradiation that causes pinholes to form in the resist films.

Crivello synthesized a series of cationic photoinitiators called onium salts that generate Brønsted acids upon irradiation and used them as PAGs for cationic polymerization of epoxy and vinyl ether monomers [27–31]. Typical examples of these onium salts include diaryliodonium and triarylsulfonium salts [32–37].

Sulfonium salts are particularly useful for nanolithography. Studies by Hacker [38–43] showed that direct photolysis of triarylsulfonium salts proceeds by predominant singlet excited state heterolytic cleavage of the C–S bond accompanied by a minor amount of homolytic cleavage. The C–S heterolytic cleavage gives phenyl cations along with diphenyl sulfide, whereas homolytic cleavage gives the phenyl radical and the diphenylsulfinyl radical cation. The reactive intermediates

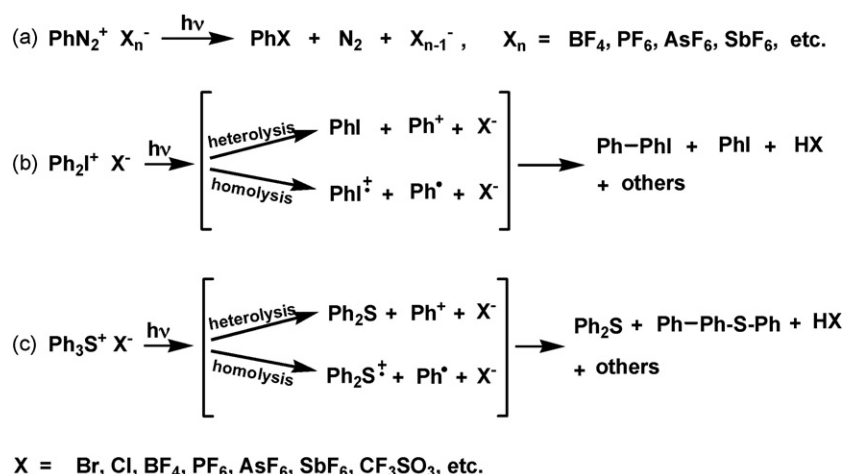


Fig. 3. Onium salt chemistry.

undergo diverse reactions to generate photoproducts as shown in Fig. 3(c). The Brønsted acid is produced both by hydrogen atom abstraction from the surrounding matrix, and from the benzene rings when activated phenyl intermediates undergo the substitution with diphenylsulfide intermediates to give Ph-Ph-S-Ph. The direct photolysis of diaryliodonium salts, although proceeding via a more complex excited state process, produces intermediates resulting from heterolytic cleavage predominantly. The paths for product formation from the reactive intermediates are analogous to those followed in the sulfonium salt system (Fig. 3(b)).

Iodonium and sulfonium salts are thermally stable (>200 °C) and nonvolatile. They also have good absorption properties at 248-nm deep UV light and good solubilities in resist films. Furthermore, they are the first known photochemical source of organic super strong acids, such as triflic acid. In addition, iodonium and sulfonium salts can be used to photochemically generate a variety of acids by changing the nature of the counter anion. Thus, easy means are available to vary the kind, acidity, volatility and size of the photogenerated acid.

There are many nonionic compounds that generate Brønsted acids upon irradiation. Particularly well known among these types of substances are *o*-nitrobenzyl esters [44] which undergo photochemically induced intramolecular *o*-nitrobenzyl rearrangement to generate nitrosobenzaldehyde and an organic sulfonic acid (Fig. 4).

Houlihan and Reichmanis synthesized a series of nitrobenzyl derivatives and used them as PAGs for nanolithographic resist materials [45–51]. While unsubstituted 2-nitrobenzyl tosylate is thermally labile at 124 °C, 2,6-dinitrobenzyl tosylate is stable up to 204 °C. Furthermore, the inclusion of sterically bulky and electron-withdrawing groups, such as CF₃, at the other ortho position of the benzyl moiety drastically increases the thermal stability of the esters (255 °C), and allows access to thermally stable esters based on powerful acids, such as triflic acid and pentafluorobenzenesulfonic acid, although precursors of such powerful acids instead of tosic acid generally have decreased thermal stability. In addition, *o*-nitrobenzyl esters have good absorption properties at 248 nm and quantum yields for their photolysis in the PMMA films range from 0.07 to 0.16.

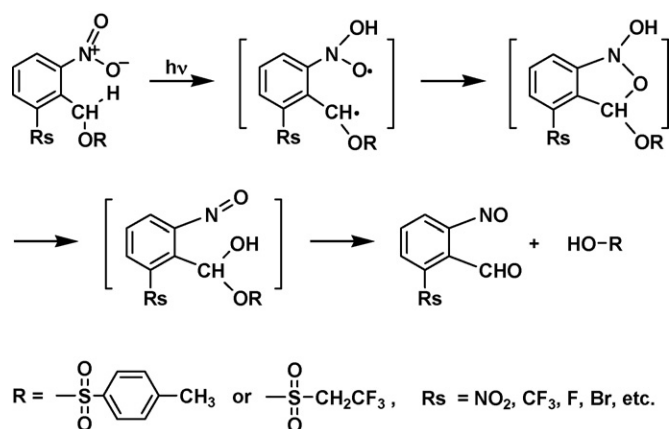


Fig. 4. *o*-Nitrobenzyl ester chemistry.

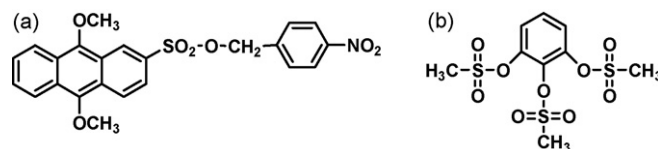


Fig. 5. *p*-Nitrobenzyl ester (a) and pyrogallol ester (b) derivatives.

Unlike their *o*-nitrobenzyl counterparts, *p*-nitrobenzyl esters do not undergo direct irradiation reactions. However, *p*-nitrobenzyl 9,10-dimethoxyanthracene-2-sulfonate (Fig. 5(a)) is photochemically transformed to 9,10-dimethoxyanthracene-2-sulfonic acid [52]. This photoreaction is a consequence of intramolecular electron transfer from the 9,10-dimethoxyanthracene moiety to the *p*-nitrobenzyl moiety. The quantum yield for the photoreaction in the acetonitrile solution is 0.08 at 254 nm and the spectral sensitivity extends to 450 nm.

Alkyl and aryl sulfonic acid esters of pyrogallol comprise an interesting group of PAGs [53–55]. As a typical example, 1,2,3-tris(methanesulfonyloxy) benzene (MeSB) shown in Fig. 5(b) exhibits no sensitivity in a non-phenolic matrix polymer. However, MeSB undergoes photochemical decomposition to produce methanesulfonic acid in a phenolic matrix resin, such as novolac. Photoresists, composed of the novolac binder, *t*-butoxycarbonyl group-protected bisphenol A and MeSB, exhibit a quantum yield for acid generation of 19.7 when irradiated with 250 nm light. Owing to the fact that three sulfonic acid ester units are attached to one ballast molecule, the highest possible theoretical quantum yield is 3. Thus, the value of 19.7 implies that acid generation from MeSB is promoted by sensitization from novolac. A spectral sensitivity of the resist is determined by the absorbed wavelength region and intensity of novolac.

DNQ derivatives act as photoactive compounds (PACs) and not PAGs. However, the 4-sulfonate form of DNQ, present in 2-diazo-1-naphthol-4-sulfonyl derivatives, can be used also as PAGs as well as PACs. As shown in Fig. 6, the initial steps in the photoreaction of DNQ-4-sulfonates give an indene-3-carboxylic acid III in the same way as does the reaction of DNQ-5-sulfonates. One of the indene ring hydrogens is nearly as a strong acid as sulfonic acids and much stronger than the carboxylic acids. This allows ArOH elimination and the formation of the sulfene derivative VI. Subsequent hydrolysis forms a free indene-4-sulfonic acid VII, capable of generating two protons per molecule [15,17,56,57].

Another group of PAGs are based on diazomethane chemistry. For example, photolysis of sulfonyl diazomethane I, shown in Fig. 7(a) [58,59], brings about Wolff-type rearrangement in the same way as for DNQ-sulfonates. Reaction either by a two-step pathway through an intermediate carbene or a concerted route leads to a highly reactive sulfene, which affords a sulfonic acid product IV. The main photolysis product (>80%) is the compound VI, probably formed via the path shown in Fig. 7(a). Although compound VI is not acidic, owing to its thiosulfonic acid ester structure it undergoes a thermally induced acid or base catalyzed decomposition reaction to yield a sulfinic acid, which in turn decomposes at an elevated temperature to a sulfonic acid (Fig. 7(b)). This reaction sequence is especially

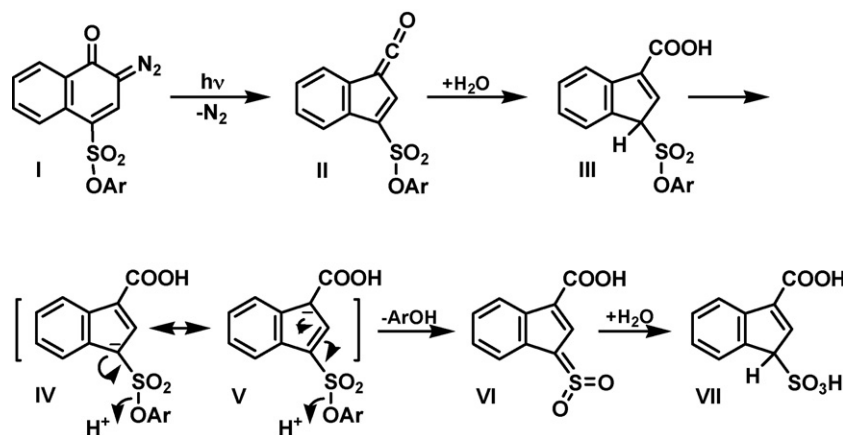


Fig. 6. DNQ-4-sulfonate chemistry.

effective in a solid matrix of a resist film when the postexposure bake is conducted. The quantum yield for the acid production in the poly(4-hydroxystyrene) film is about 0.27 at 254 nm. Several examples of diazomethane-based PAGs are shown in Fig. 7(c).

A class of halogenated organic compounds has been used as a PAG. A typical example includes halomethyl-*s*-triazines [57,60,61]. As can be seen from Fig. 8(a), halomethyl-*s*-triazines are capable of acting both as a free-radical photoinitiator and a PAG. They produce halogenic acids on irradiation and exhibit absorption maxima between 335 and 495 nm. They also give quantum yields ranging from 0.29 to 0.35 in novolac films. In addition, as can be seen from Fig. 8(b), disulfone compounds are an efficient PAG. They produce sulfinic acids on deep UV irradiation, with a rapid absorption bleaching. They also show absorption maxima in the range of 255–338 nm [62].

3.2. Polarity change mechanism for deep UV photoresists

The minimum resolution in nanolithography improves with a decrease in the wavelength of the irradiation light. As a result, new photoresists exhibiting high sensitivity and comprised of a binder transparent to the reduced wavelength are needed. However, conventional novolac/DNQ resists do not meet such a prerequisite, due to their relatively low sensitivity and the deep UV opacity of novolac.

Several strategies to solve this problem incorporate a poly(*p*-hydroxystyrene) (PHS) binder which is transparent to deep UV (>70 %/μm). In addition, a chemical amplification concept based on a polarity change mechanism promoted by an acid-catalyzed deprotection of acid-labile groups has made high performance deep UV photoresists feasible. *t*-Butoxycarbonyl (*t*-BOC) groups is an important acid-labile blocking group for

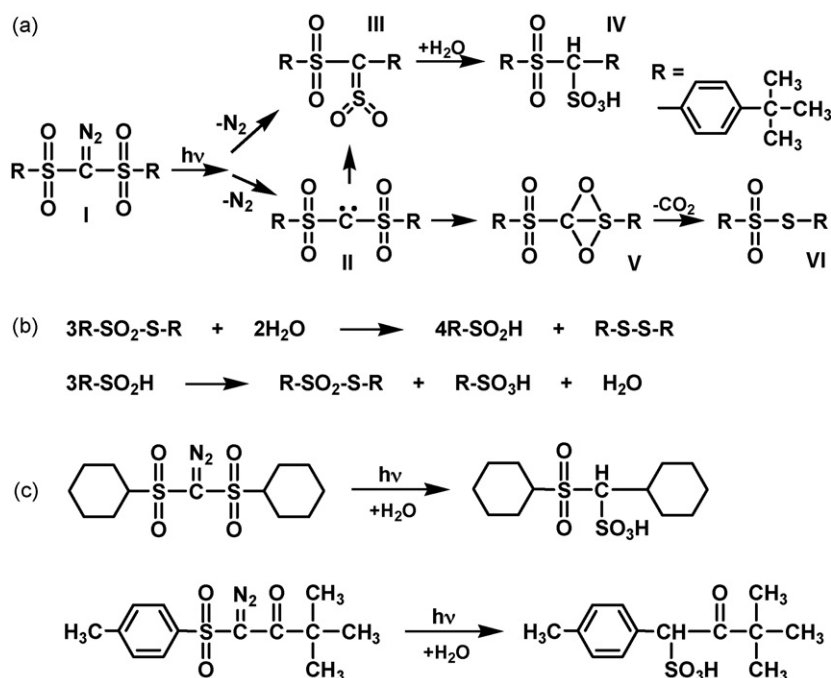
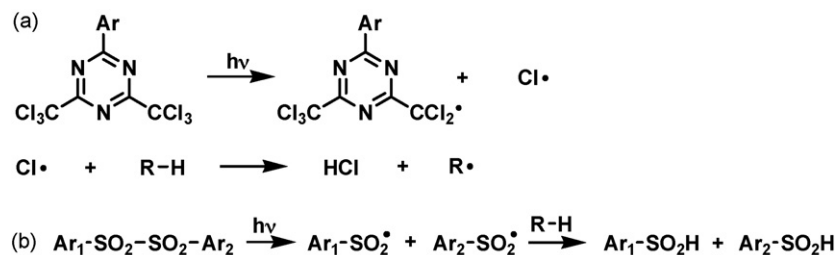
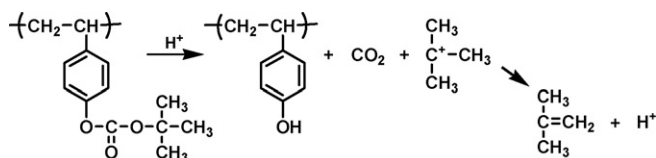


Fig. 7. Photochemistry of diazomethane derivatives.

Fig. 8. Photochemistry of halomethyl-*s*-triazines (a) and disulfone compounds (b).Fig. 9. Acid-catalyzed deprotection of *t*-BOC-protected PHS resists.

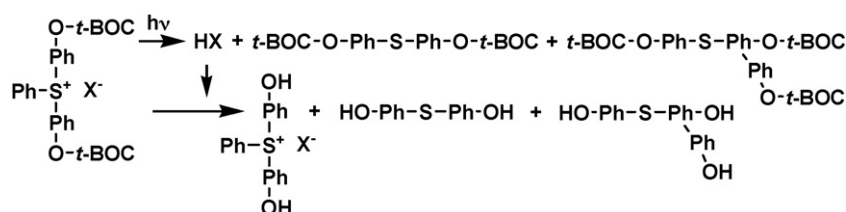
use in acid-promoted deprotection-type photoresists. The initial study by Ito, Willson and Fréchet [4–6,63,64] was performed by using poly(*t*-butoxycarbonyloxystyrene) (PBOCS), obtained by blocking PHS with acid-labile *t*-BOC groups. Resist films are composed of lipophilic PBOCS and a PAG. Upon irradiation, acids photogenerated from a PAG catalytically cleaves *t*-BOC groups during postexposure bake (PEB) at high temperature as shown in Fig. 9. Consequently, the lipophilic PBOCS converts to the hydrophilic PHS along with the regeneration of acids, and thus chemical amplification is accomplished. Since the hydrophilic PHS in the exposed area is soluble in an aqueous base or a polar organic solvent and insoluble in a non-polar organic solvent, this system shows dual-behaviour dependent on the developer polarity. Accordingly, PBOCS films after irradiation and subsequent PEB exhibit positive-working behaviour in an aqueous base developer and negative-working behaviour in a non-polar organic developer.

Schwalm et al. reported a new type of resist based on triarylsulfonium salts containing *t*-BOC groups in the side chain. Triarylsulfonium salts blocked with *t*-BOC groups are an effective dissolution inhibitor as well as PAG. The resist containing this sulfonium salt photochemically decomposes to produce acids which catalytically cleave pendant *t*-BOC groups after PEB. All of the photoproducts are changed to hydrophilic phenolic products capable of accelerating dissolution, and consequently a positive mode resist with high sensitivity is obtained in an aqueous base developer (Fig. 10) [65,66].

Acetals are also important blocking groups that have been used for acid-catalytic deprotection-type photoresists. An inter-

esting report describes acid-catalyzed decrosslinking of acetal crosslinks. A typical example of this strategy is a two-component photoresist consisting of a PHS binder bearing vinyl ether groups in the side chain and a PAG [67,68]. The pendant vinyl ether groups react with hydroxyl groups of the binder through an electrophilic addition reaction to form acetal crosslinks, when the spin-coated resist films are prebaked at relatively high temperatures. The crosslinks are catalytically cleaved by acids after exposure to light followed by PEB to give phenolic and aliphatic alcohols, and acetaldehyde. Consequently, positive-working patterns are obtained in an aqueous base developer (Fig. 11(a–b)). Urano et al. described a series of commercially important photoresists based on an acid-catalytic decomposition of the PHS protected with pendant open-chain acetals (Fig. 11(c)) [52]. These acetals include 1-ethoxyethoxy, 1-methoxyethoxy, 1-methoxy-1-methylethoxy, 1-butoxyethoxy, and 1-benzyloxy-1-methylethoxy groups. In Fig. 11(d) is shown an acid-catalyzed decomposition process of PHS resists bearing cyclic acetals in the side chain. The representative examples include tetrahydropyranyl and tetrahydrofuranyl groups [69,70].

Pawlowski et al. reported the three-component photoresist consisting of poly(3-methyl-4-hydroxystyrene-co-hydroxystyrene) binder, a PAG and an oligomeric O–C–O or O–C–N group-based dissolution inhibitor [71–73]. The poly(3-methyl-4-hydroxystyrene) binder was synthesized by modifying PHS for dissolution inhibitor type resists [74]. Acetal derivatives are hydrophobic and act as dissolution inhibitors through their physical interaction with a phenolic binder to give the insoluble resist film in an aqueous base developer. Acids photogenerated from a PAG using 248 nm light catalytically cleave acetal groups during PEB to give hydrophilic alcohols and an aldehyde. Consequently, a dissolution inhibiting effect in the exposed areas disappears, offering a positive-working resist in an aqueous alkali developer (Fig. 12). In addition, other acid-labile group-blocked binder polymers and dissolution inhibitors that have been used in two- and three-component photoresists are shown in Fig. 13(a) [75–77] and (b) [78–79], respectively.

Fig. 10. Photochemistry of *t*-BOC-blocked triarylsulfonium salts.

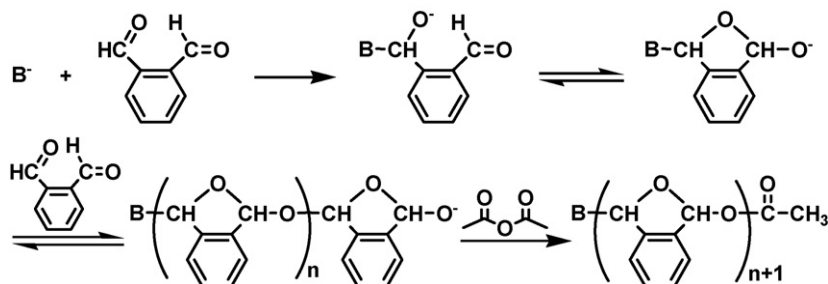


Fig. 14. Anionic polymerization of phthalaldehyde.

3.3. Depolymerization mechanism for deep UV photoresists

Another approach to chemical amplification employs acid-catalyzed depolymerization. Initial studies of this strategy focused on depolymerization of polyphthalaldehyde (PPA) [5,80,81]. PPA, synthesized by anionic polymerization in a reversible equilibrium reaction (Fig. 14), has good dissolution properties in organic solvents. PPA has a low ceiling temperature (-40°C) that is below room temperature. The polymerization process can be carried out at cryogenic temperatures but the polymer rapidly depolymerizes to form monomer when isolated at room temperature. However, if these polymers are end-capped by acylation or alkylation prior to isolation, they are stable up to 250°C . End-capped PPA undergoes depolymerization upon irradiation with deep UV light. The process involves photocleavage

of one acetal bond in the main chain, followed by spontaneous depolymerization (unzipping process), thereby serving as a chemically amplified self-developing positive-working resist. Unfortunately, exposure of the polymer alone does not provide clean self-development. Sensitization of PPA by using an onium salt PAG, achieves acid-catalyzed cleavage of the main chain acetal bonds and provides highly sensitive self-developing positive-working resists ($<2.5\text{ mJ/cm}^2$). A drawback of PPA is its poor plasma-etching resistance and the production of a gaseous aldehyde, which contaminates the optics of the exposure tool.

Polycarbonates containing carbonate groups in the main chain undergo thermal or acid induced depolymerization. In Fig. 15(a) is shown a photo-labile polycarbonate, terpolymerized with *o*-nitrobenzylglycidyl ether, propylene oxide and

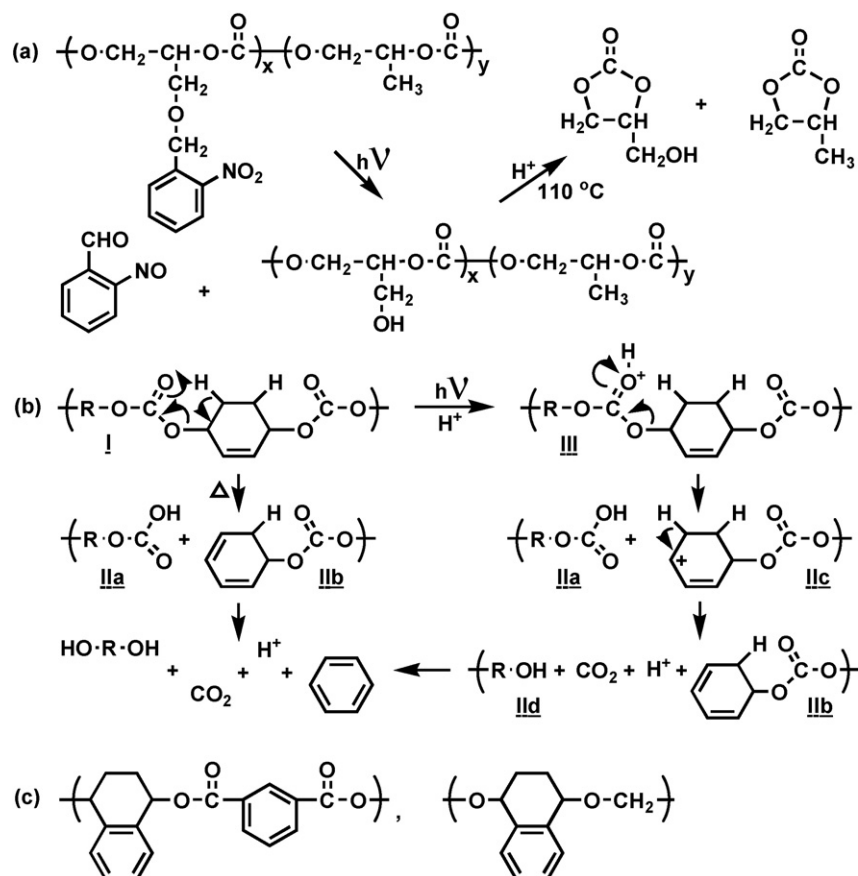


Fig. 15. Depolymerization of polycarbonates.

carbon dioxide [80]. UV irradiation of these terpolymers, containing up to 50% of the photosensitive *o*-nitrobenzyl group, results in the clean removal of the *o*-nitrobenzyl protecting groups and concurrent liberation of the polycarbonate containing free hydroxymethyl groups. This hydroxymethyl polycarbonate is thermally stable up to 200 °C, but in the presence of acid depolymerization of this material in the solid state occurs at 110 °C. Another example of the polycarbonate depolymerization [82–84] is given in Fig. 15(b). This polycarbonate I, consisting of 2-cyclohexenyl carbonate groups in the main chain, undergoes thermolytic cleavage through a *cis*-elimination pathway at ca. 200 °C, while the temperature required for this process is reduced when an acid is present. The reaction is initiated by protonation of a carbonyl group to afford III, which undergoes cleavage of the neighboring allylic C–O bond to produce a monoester of carbonic acid IIa and an allylic carbocationic moiety IIc. Elimination of a proton from this carbocationic moiety results in regeneration of the acid catalyst and formation of a diene-containing fragment IIb. The unstable monoester of carbonic acid IIa decarboxylates releasing an alcohol fragment IIc. The process continues at other carbonate sites leading to complete breakdown of the polymer chain resulting in the eventual release of benzene, additional carbon dioxide, and a diol. Consequently, the system serves as a self-developing type positive-working resist without the need for a development step. Examples of other depolymerizable polyester and polyether are shown in Fig. 15(c) [82–84].

Poly(α -methylstyrene) derivatives also undergo acid-catalyzed depolymerization caused by backbone scission (Fig. 16) [85–89]. A representative example is cationically polymerized poly(*p*-hydroxy- α -methylstyrene) (pPHOMS), which exhibit ca. 50% thickness loss upon irradiation and subsequent PEB. In contrast, the *meta*-isomer shows only 2–3% thickness loss and anionically polymerized pPHOMS is inert to acidolysis. These results are consistent with the operation of a pathway involving depolymerization beginning and propagating from the

terminal end of the polymer chain. The anionic pPHOMS has very stable end groups including alkyl moieties that derive from alkyllithium reagents used in their formation and hydrogens coming from protonation of the growing anion. Thus, photogenerated acids do not react with pPHOMS produced by anionic polymerization. However, cationically polymerized pPHOMS have either OH or OCH₃ end groups, formed by termination with water and methanol, or β -methylstyryl end groups generated by deprotonation of a carbocation. The alcohol, ether and β -methylstyryl end groups undergo acidolysis to produce terminal carbocations, which undergo depolymerization on heating. In particular, when the electron-donating *p*-OH substituent is present to stabilize the carbocation depolymerization is facile.

3.4. Crosslinking mechanism for deep UV photoresists

Initial studies of chemically amplified photoresists concentrated on cationic polymerization mechanism as represented by ring-opening polymerization of epoxy resins, affording negative-working images in an organic solvent developer [5,25–27,90,91]. However, the employment of an organic solvent as a developer causes swelling of the resist pattern and results in lower resolution. Resolution lowering caused by swelling can be avoided by developing an acidic phenolic resin-based resist in an aqueous base solution. A new family of negative-working resists based on acid-catalyzed crosslinking of phenolic resins have been reported [92–95].

The swelling-free resist, based on an electrophilic aromatic substitution chemistry, is comprised of a phenolic copolymer containing a latent benzylic electrophile and an electron-rich arene along with a PAG. As shown in Fig. 17(a and b), the electrophilic benzylic carbocation that is liberated by the photogenerated acid undergoes reaction with the arene by either C- or O-alkylation to form crosslinks and regenerate acid. This system can be also extended to a three-component resist composed of a phenolic binder, a latent polyfunc-

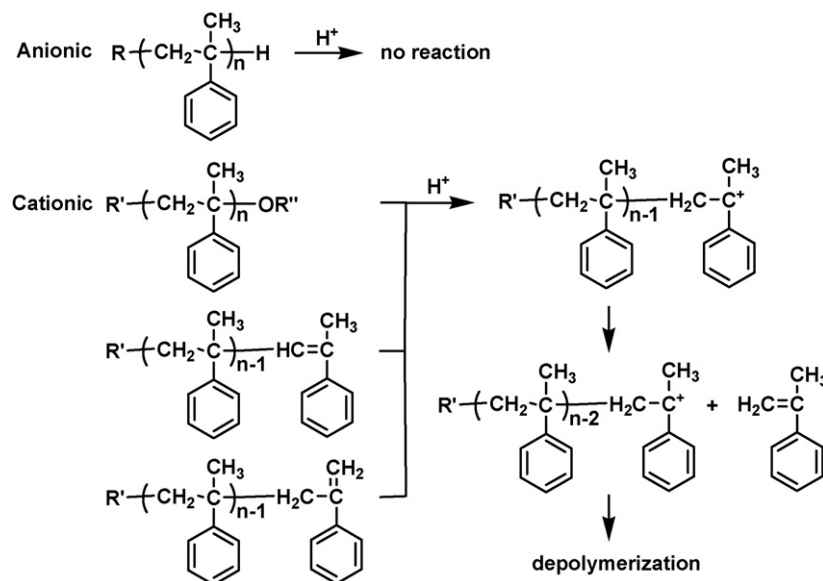


Fig. 16. Acidolytic depolymerization of poly(α -methylstyrene) derivatives.

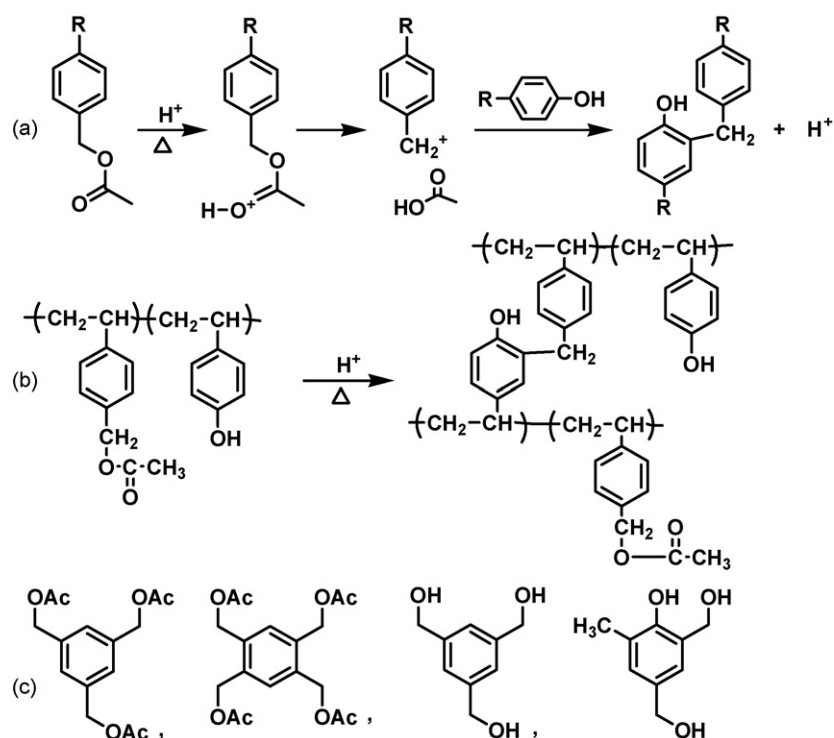


Fig. 17. Acid-catalytic crosslinking based on electrophilic aromatic substitution.

tional electrophile, and a PAG [96,97]. As can be seen by viewing Fig. 17(c), latent electrophiles contain benzylic moieties blocked with acetoxyl or hydroxyl leaving groups in the structure.

Another type of three-component photoresist based on electrophilic substitution chemistry is composed of a phenolic binder, a *N*-methoxymethylated melamine crosslinking agent and a PAG [60,98–100]. In this system (Fig. 18), the photo-generated acid reacts with the melamine derivative to produce carbocation, which undergoes an electrophilic substitution at arene ring sites or hydroxyl groups of the phenolic binder to form crosslinks and regenerate acids. In this way, the process gives acid-catalyzed negative-working images with high sensitivity and resolution. These resists exhibit resolutions of 0.3 μm line and space under 248 nm KrF excimer laser and 0.1 μm line with electron beam.

3.5. Polarity change mechanism for 193 and 157 nm irradiation

The drive toward still smaller features led to research and development of high-resolution single-layer resists suitable for 193 nm exposure using an ArF excimer laser as the light source. Deep UV resists using a 248 nm KrF excimer laser cannot be used at 193 nm owing to the high absorption at 193 nm of their aromatic chromophores. PHS-based matrix resins described in the above section are completely opaque at 193 nm. In contrast, aliphatic methacrylate copolymers have low absorption at 193 nm.

Initial studies of 193 nm resists were conducted using the poly(methyl methacrylate) terpolymer shown in Fig. 19 [101–103]. These resists are composed of the terpolymer containing an acid-labile *t*-butyl methacrylate repeat unit and a PAG.

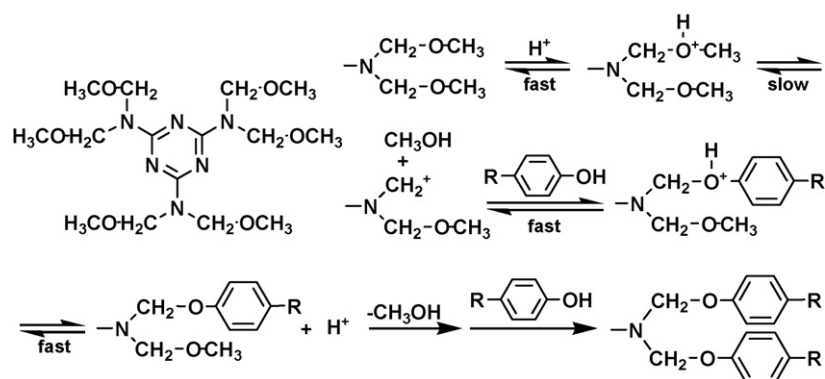


Fig. 18. Acid-catalytic crosslinking through O-alkylation of melamine derivatives.

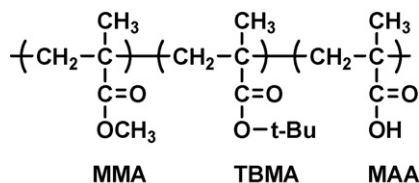


Fig. 19. Poly(methyl methacrylate)terpolymer-based resists. MMA: hydrophilicity control and adhesion, TBMA: polarity change based on acid-catalyzed deprotection, MAA: aqueous alkali developability.

While transparent at 193 nm and exhibiting excellent resolution, these resists have low plasma-etching resistances. The plasma-etching stability of aromatic polymers, such as novolac or PHS, comes from their high effective carbon content [104]. Thus, the higher the carbon content and the lower the oxygen content, the more resistant they are to an etching plasma. On the basis of this correlation, the introduction of an alicyclic moiety, such as adamantyl or norbornyl into the structure is necessary in order to obtain a suitable plasma-etching resistance [105–113]. The incorporation of alicyclic groups can be achieved in two ways: (i) the incorporation of alicyclic groups into the pendant side chain and (ii) the direct incorporation of alicyclic structures into the polymer backbone.

A typical polymer having the former features is a copolymer composed of an adamantyl methacrylate moiety as an etching resistance unit and a 3-oxocyclohexyl methacrylate moiety as an acid-labile component (Fig. 20(a)) [114]. Poly(adamantyl methacrylate (AdMA)-co-3-oxocyclohexyl methacrylate (OCMA)) containing 60% of a pendant adamantyl group exhibits almost the same dry etch resistance as novolac and the high transparency of 70 %/μm at 193 nm. Also, the acid-labile OCMA group easily decomposes in the presence of an acid, because the acidic ketone α-proton, especially when it is on a ring antiperiplanar to the C–O bond, is easily eliminated.

Nevertheless, the poly(AdMA-co-OCMA)-based photore-sists containing a PAG do not exhibit good developability in 2.38 wt% aqueous solution of tetramethylammonium hydroxide (TMAH).

In order to achieve good developability under these conditions, it is necessary to have either an OCMA group that is more rapidly deprotected or an AdMA group that has new deprotection capability. The adamantyl ester in AdMA has a tertiary carbon structure, but it is not readily cleaved by acids, because the resulting alkene would be part of a highly strained ring system. However, a 2-methyl-2-adamantyl group can easily produce an exocyclic double bond and, as a result, it should be smoothly cleaved in the presence of acids (Fig. 20(b)) [115]. The deprotection capability of the 2-methyl-2-adamantyl group was found to be almost the same as that of the *t*-butyl methacrylate (Fig. 19). The introduction of either mevalonic lactone or 3-hydroxy-γ-butyrolactone instead of 3-oxocyclohexyl group causes the ester to be too easily decomposed in the presence of an acid and matches their ester to the 2-methyl-2-adamantyl ester very well (Fig. 20(c)) [116,117]. Photore-sists based on each copolymer shown in Fig. 20(c) exhibit the best lithography performance including high sensitivity and resolution at 193 nm.

On the other hand, in later designs of 193 nm resists, alicyclic structures were incorporated directly into the polymer backbone [106–112]. It is preferred that the alicyclic backbone polymers be synthesized by using free-radical polymerization of cycloolefins rather than by using metal-catalyzed or metathesis polymerization from a consideration of the potential metal ion contamination.

Polymers having 1:1 alternating structures are made by copolymerizing cyclic olefins with maleic anhydride under free-radical conditions. A typical example based on norbornene-maleic anhydride copolymerization is shown in Fig. 21 [118–121]. In order to enable aqueous base solubility, acrylic

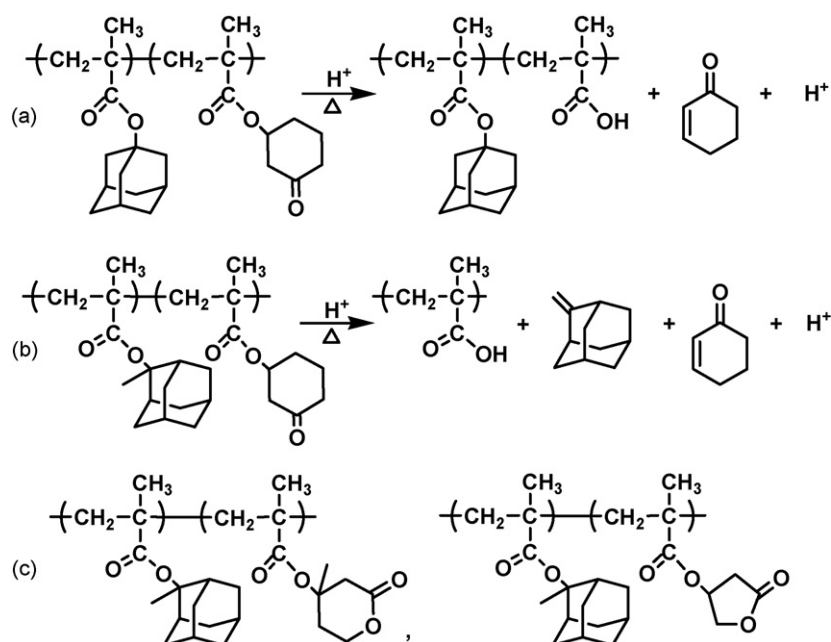


Fig. 20. Adamantyl methacrylate copolymer-based resists.

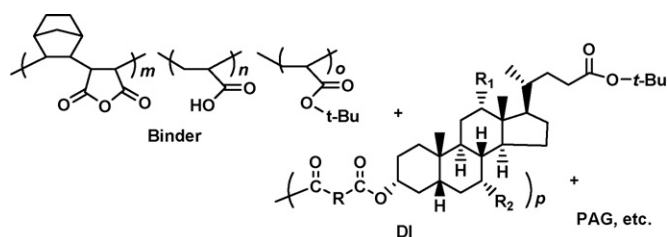


Fig. 21. Norbornene-maleic anhydride-based resists. DI: dimeric or oligomeric (the average degree of polymerization: 5–40) dissolution inhibitor.

acid and its acid-labile ester derivatives were incorporated into the polymer main chain, as shown in Fig. 21. Since acrylic acid-based resists dissolve much more rapidly in the aqueous base developers than their phenolic counterparts, pattern-images are deteriorated because of greatly varying dissolution rates in exposed areas and unexposed areas. As a result, a dissolution inhibitor is necessary for finely tuning the dissolution rate. *t*-Butyl cholate-based dimeric and oligomeric dissolution inhibitors used for this purpose are transparent at 193 nm and are bulky and highly soluble in the matrix polymer. Typical resist films of this type containing a PAG are capable of resolving 80 nm patterns with phase-shift mask technology.

The most advanced production lines for nanofabrication of semiconductor devices now operate at 193 nm. Further reduction in the wavelength of the irradiation light to 157 nm from a F₂ excimer laser necessitates construction of a new resist material platform [122–126]. Most organic materials, air, and water are opaque at 157 nm. The best alicyclic resins designed for 193 nm resists also show high absorbance of ca. 2 μm^{-1} at 157 nm [127]. Based on the fact that the absorbance of the adamantane-based resin (Fig. 20(c)) is only 0.22 μm^{-1} at 193 nm [128], it is clear that a new resin design with a low absorbance at 157 nm is needed.

The incorporation of fluorine atoms into a resin structure renders them relatively transparent at 157 nm absorption. In Fig. 22(a) are shown several 157 nm resin samples [127,129,130]. Norbornene copolymer I, containing geminal trifluoromethyl groups and produced by vinyl addition, has an absorbance of 2.3 μm^{-1} . This is a better transparency than that of poly(norbornene), but still too high to be useful. In addition, the absorption of norbornane depends not only on the number of fluorines substituted on the norbornane ring, but also more importantly on the position of the substitution. Norbornane II, difluoro-substituted in the 2 position on the ring, shows the low-

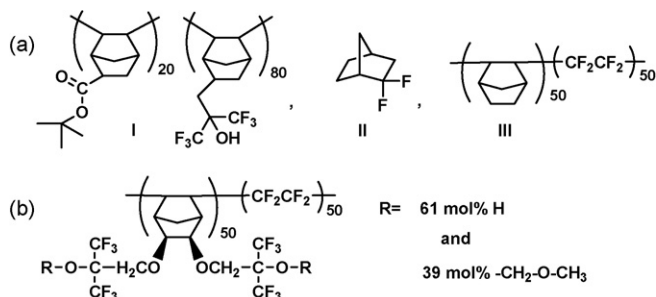


Fig. 22. Fluorinated polynorbornane-based resists.

est absorption at 157 nm. Fluorinated norbornene monomers also undergo strictly alternating free-radical copolymerization with tetrafluoroethylene to afford the model structure III, which has the relatively low absorbance of 1.1 μm^{-1} . These results present important clues for the design of new high performance 157 nm photoresists.

Recently, there is an interesting report (Fig. 22(b)) [131,132] based on the model structure III. The incorporation of two fluoroalcohol groups into the norbornene structure leads to a remarkable increase in dissolution rate. A norbornene monomer bearing two pendant hexafluoro-2-propanol groups on the exo face was synthesized and then copolymerized with tetrafluoroethylene by using free-radical polymerization to give a 1:1 alternating structure. The fluoroalcohol groups are partially protected with methoxymethyl groups to give an acid-labile acetal structure. The employment of an acetal group as a protecting group helps increase transparency at 157 nm, since carbonyl group-based protecting groups such as a *t*-BOC group have strong absorption at 157 nm. The resulting copolymer, shown in Fig. 22(b), has a very low absorbance of 0.59 μm^{-1} at 157 nm. The 220-nm thick resist films containing a sulfonium salt also demonstrated 80 nm 1:2 lines at the same wavelength.

3.6. Resists for next generation lithography

The above-mentioned approaches to optical lithography cannot resolve feature sizes below 50 nm. As a result, new strategies will be needed in order to reach this goal. Promising candidates for this purpose include extreme-UV (EUV) lithography (or so called soft X-ray lithography), X-ray lithography, electron-beam (E-beam) lithography, and ion-beam lithography. These technologies are based on the use of high-energy photons (0.5–13 nm) and high-energy charged particles (electrons or ions) and they will require the development of new families of photoresists.

EUV resists, mainly using 13 nm light from hot plasmas, have been investigated for either bilayer thin film imaging or top-surface imaging since essentially all of the materials are strong absorbers in the extreme-UV wavelength region. However, the single layer resist technology is very important from the viewpoint of cost. Recent reports have described EUV absorption at 13 nm [133,134] and have shown that (1) polymers with low density show low absorption, (2) absorption varies directly with the oxygen content, (3) silane polymers have the lowest absorption, and (4) the incorporation of aromatic rings into a polymer structure reduces the absorption. A typical PHS-based resist showed 60% transparency at 135-nm thickness, implying that a possibility for success exists. These results suggest that a suitable match of silane structures and aromatic rings may provide an acceptable single layer resist system. In addition, all the optical components of a EUV source must be reflective mirrors, not transmissive and refractive lenses.

X-ray resists mainly use 0.2–1.5 nm beams from a synchrotron source. At this short wavelength, most materials are transparent (the absorbance of typical PHS-based resists is 0.12 μm^{-1} at 1 nm, while their absorbance at 248 nm is 0.18 μm^{-1}) [128]. Also, when a synchrotron source is

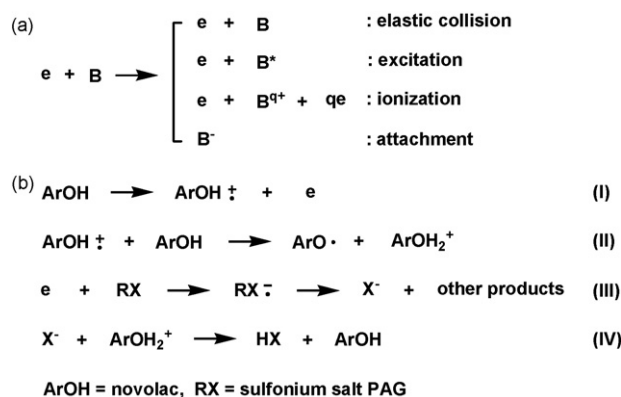


Fig. 23. Radiochemistry of X-ray and E-beam resists.

employed, a highly collimated beam is emitted. Such properties enable the use of X-ray single layer resists, but no focusing optics is employed only allowing 1:1 proximity irradiation.

For 100 kV E-beam and 75 kV He^+ ion beam, the absorbance of typical PHS-based resists is 0.02 and $3.7 \mu\text{m}^{-1}$, respectively, based on results calculated only for comparison purposes since the “optical density” concept is not used for charged particles [128]. The E-beam shows high transmittance. Furthermore, absorbance is less important for the high-energy charged beam and high-energy X-ray, because the penetration depth is changed according to acceleration voltage. Also, each range of photoelectrons and secondary electrons is sufficiently high, and radiochemistry accompanies a number of sensitization processes.

As light from an optical source is changed to the high energies of X-rays or charged beams, the working mechanism in resist films is changed from an excitation to an ionization process. When accelerated high-energy X-rays or charged beams collide with molecules or atoms, photoelectrons or secondary electrons are released and radical cation intermediates are formed (ionization process). The intermediates and the surrounding electron-rich species that accept the released electrons undergo fragmentation and simultaneously react to afford more diverse products than those that are produced in photochemical reactions. Resist radiochemistry consists mainly of ionization processes, along with additional excitation, electron exchange, electron attachment, elastic collision and charge transfer, etc. An example of the events taking place when accelerated electrons collide with atoms is shown in Fig. 23(a) [135,136].

There are a series of reports concerning X-ray- and E-beam-induced acid generation in chemically amplified resist films [137–141]. The resists composed of partially *t*-BOC-protected novolac resin and a sulfonium salt PAG were irradiated with 0.7 nm synchrotron X-rays and E-beams and studied by assigning intermediates by using both nano- and picosecond pulse radiolysis. X-ray or E-beam irradiation ionizes matrix novolac molecules to release electrons (Fig. 23(b-I)). The ionized novolac molecules protonate the neighboring molecules (Fig. 23(b-II)). The sulfonium salts scavenge the released electrons to give dissociated anions (Fig. 23(b-III)), which recombine slowly with the protonated molecules to afford

Brønsted acids (Fig. 23(b-IV)). This matrix ionization path accounts for 93% of the total reaction, followed by direct excitation of sulfonium salts of 5% and others.

In order to obtain acceptable radiation resists, such complex reactions in resist films have to be sufficiently understood and controlled, along with improvement in resist sensitivity more than 10 times in comparison to the current systems. In addition, next generation radiation resists must be capable of producing images with low line-edge roughness (LER). LER as the measure of random fluctuation in the width of a resist feature becomes highly important in the sub-50 nm feature size regime, because the dimensional tolerances from the predicted line-edge of the minimum dimensions of resist patterns approach the scale of the molecular components of the films. Molecular glass photoresists are a recent advance for resolving the sub-50 nm feature sizes with the least LER. The resists contain small, monodispersed amorphous glass molecules with high T_g , instead of conventional polydispersed amorphous polymer binders. [G-2] and [G-3] dendrimers based on a hexavalent core derived from 1,1,1-tris(hydroxyphenyl)ethane [142], tri-substituted aromatic cored compounds such as 1,3,5-tris[4-(*t*-butoxycarbonylmethoxy)-phenyl]benzene [143–146], calixarene derivatives [16,147,148,149], and polyhedral oligomeric silsesquioxanes [150] are good examples of such molecules. The resists containing such molecules afforded positive- or negative-working patterns, depending on the kind of both incorporated functional groups (either *t*-BOC acid-labile group or crosslinking agents) and employed developers (either an aqueous base or an organic solvent).

4. Conclusion

The continuing requirement for high performance photoresists with high sensitivity and high resolution led to the development of the chemical amplification concept in resist systems. In chemically amplified resists, one photochemical event leads to a cascade of subsequent reactions. Chemical amplification is accomplished through acid-catalyzed polarity change, depolymerization by unzipping process, or the acid-catalyzed crosslinking mechanism. In general, the resolution of photoresists improves as the irradiating wavelength decreases. As a result, there has been a gradual shift in the focus from 436 and 365 nm to 248 and 193 nm. The most advanced production lines for nanofabrication of semiconductor devices now operate at 193 nm. Further reduction in wavelength necessitates the employment of 157 nm or radiation such as EUV, X-ray, and E-beam. The reduced wavelength requires the discovery of new photoresists that have chemistry promoted by irradiation at each wavelength. As pointed out in this review, research in resists and their versatile chemistry continues at a swift pace.

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