Application of polymers to photoresist materials

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1. INTRODUCTION

Recent years have seen remarkable technical innovation in mobile phones, PDAs and similar electronic equipment, with equally profound changes in the way we live. None of this would have been possible without the large scale integration and miniaturization of semiconductor integrated circuits, a transformation underpinned by developments in microfabrication technology. Advances in photolithographic technology in particular have played a pivotal role, matched by the development of photoresist materials based on the polymers best suited to the successive technologies. This review outlines the historical development of photoresist materials, with an account of successive generations of photoresist under separate headings.

2. The evolution of photoresist materials

As used in LSI production lithography, “photoresist” denotes a polymer material in which photochemical (or radiochemical) reaction occurs and whose rate of dissolution by a developer solution varies according to the energy distribution created by ultraviolet light, x-rays or electron beam exposure, allowing the formation of a resist pattern. The resist is said to be positive when the exposed regions are removed by the developing process and negative when, conversely, the exposed regions are left intact by the developing process [1].

Figure 1 maps the chronological development of lithography and resist materials [2]. The wavelength initially used for photolithography in the 1980s was the visible emission g-line (436 nm) from the high pressure
mercury lamp, followed by the i-line (365 nm). With the trend towards shorter wavelengths, the KrF excimer laser (248 nm) and ArF excimer laser (193 nm) were later adopted, giving wavelengths still in use today [3, 4]. Much research has also been done on high energy beams such as electron beam and extreme ultraviolet (EUV, 13.6 nm) radiation, of which the latter in particular is viewed as the most likely candidate for the next-generation of lithographic technology.

Normally, to form a pattern on the resist film, the light must be able to penetrate easily through the film to the underside. The resist material best suited to the exposing wavelength must therefore be identified. Figure 2 shows the relation between light absorption and exposure wavelength for the base resins typical of successive generations of photoresist.

The material used for the g-line (436 nm) and i-line (365 nm) wavelengths in the ultraviolet region in stepper exposure is a resist comprising a novolac base resin and a sensitizer consisting of a 1,2-naphthoquinone diazide sulphonate ester (NQD). To make use of the KrF (248 nm) line in the extreme ultraviolet region, the photoresist changed to the chemical amplification type with polyhydroxystyrene (PHS) as its base resin [5]. Since the benzene ring skeleton of novolac resins and PHS absorbs a lot of light at around 200 nm, exposure with ArF (193 nm) required the development of a new base resin [6]. A polymer that has an alicyclic ring (adamantane or norbornene) of low light absorption instead of a benzene ring is employed as the base for an ArF photoresist. Photoresist materials typical of each generation are summarised in Figure 3.

Further shortening of the wavelength of the exposing light is one way of achieving higher resolution, and at one time F2 laser beam exposure (157 nm) attracted much investigation. Light absorption in the 157 nm region demands a more careful approach, and attention focussed on fluorine-containing polymers and polysiloxanes of low absorption in the 157 nm region [7]. However, development of the optical materials and lens presented difficulties and attempts at practical application were abandoned. Instead, the use of a higher numerical aperture (NA) was investigated as another means of increasing resolution. High NA was attained by wet immersion technology using a liquid (pure water) between the wafer and lens of the exposing apparatus, and a resolution of 50 nm or less has been realised. Further downscaling is being pursued and EUV (13.6 nm) lithography is under development [8]. More recently interest has turned to UV nano-imprint lithography utilising pattern fabrication technology [9], directed self assembly technology as a patterning method using the self-organization of polymers, and other bottom-up techniques [10].

![Figure 2. Light absorption of base resins typical of successive generations of photoresist](image)

![Figure 3. Photoresist materials representative of different exposure wavelengths](image)
2.2 The birth of semiconductor photoresists

The first photoresist produced for semiconductor application is considered to be poly(vinyl cinnamate), a negative resist. As shown in Figure 4, poly(vinyl cinnamate) cyclizes upon exposure to wavelengths up to around 300 nm owing to dimerization of the cinnamate group. The cyclization reaction interlinks the polymer molecules to form a three-dimensional network structure, rendering the exposed polymer insoluble in the developer.

The next photoresist to be developed was a rubber-based negative resist. As shown in Figure 5, this had two main components: a base resin of rubber and an azide. The base resin was a cyclized polyisoprene or cyclized polybutadiene obtained by acid-catalysed cyclization of polyisoprene or polybutadiene. A bisazido-compound, containing two azide groups, was commonly used as the photosensitizing agent for negative photoresists and crosslinked the non-photosensitive cyclized rubber, rendering it insoluble in the developer. To serve as a base resin, the rubber polymer typically had to have strong resistance to acids and alkalis, combined with good adherence to diverse substrates. However, the downscaling achievable with negative photoresists comprising cyclized rubber and bisazide compound was limited by the swelling that occurs during development.

2.3 Novolac resin-naphthoquinone diazide type photoresist

To achieve further downscaling, a positive photoresist was developed comprising novolac resin and 1,2-naphthoquinone diazide sulphonate ester (NQD), which inhibited the swelling response during developer treatment. The switch from a negative photoresist comprising cyclised rubber and bisazide to this positive resist did not simply entail a change in type from negative to positive; it also entailed a change from developing with organic solvent to developing with aqueous alkali solution. The resin (novolac) obtained by condensing a phenolic compound with formaldehyde using an acid catalyst is soluble in alkali solution by virtue of the phenolic hydroxyl groups present. On the other hand, the photoresist film comprising a mixture with hydrophobic NQD is insoluble in aqueous alkali solution. On exposure with the g-line or i-line, the photodegradation shown in Figure 3 proceeds in the exposed area and the NQD compound that renders the novolac resin insoluble in aqueous alkali solution decomposes. The hydrophilic indenecarboxylic acid formed by photochemical reaction dissolves in aqueous alkali solution, promoting the solubility of the novolac resin in the solution. A positive pattern can hence be obtained owing to the difference in solubilities in alkali solution created by exposure. The resist is still used for forming patterns with dimensions of 0.3 µm order using g-line or i-line reduced projection type exposure equipment (stepper). The imaging mechanism for a positive photoresist of a novolac-NQD compound is here shown schematically in Figure 6 [11].

The strong interaction in the resist film between the NQD compound and the hydroxyl groups in the novolac resin stops the novolac from ionising and thus dissolving in the aqueous alkali developer. The NQD compound itself is insoluble in alkaline developer but on exposure it photodegrades to indenecarboxylic acid, which is soluble in the developer. Because of its hydroxyl groups, the novolac base resin is soluble in the alkaline developer and unless there is interaction with the NQD compound, therefore, it remains soluble in the alkaline developer and so the exposed resist as a whole dissolves in the

![Polyvinyl cinnamate](image)

**Figure 4.** Cyclization of poly(vinyl cinnamate) by exposure to light

![Cyclic isoprene rubber and bis-azide](image)

**Figure 5.** Rubber-based negative photoresist
The key factor is the solubility difference of the resist film before and after exposure, a large solubility contrast being desirable. However, formation of a pattern by expressing the chemical changes in the NQD sensitizer as a physical change in properties, namely solubility in alkaline developer, has imposed limits on resolution.

2.4 Chemical amplification type photoresists for KrF excimer laser exposure

Lithographic exposure equipment using a KrF excimer laser instead of the g- or i-line utilised a narrower excitation bandwidth; the exposure intensity was therefore weaker than in g- and i-line exposure, requiring a photoresist of high sensitivity. To increase sensitivity, Ito and co-workers at IBM proposed a chemically amplified photoresist utilising acid-catalysed reaction in which exposure generates an acid [12]. The concept of the chemically amplified photoresist is shown in Figure 7. The acid generated by exposure acts as a catalyst that prompts multiple cycles of chemical reaction (deprotection) in response to heat. The polyhydroxystyrene formed on deprotection undergoes a change in solubility in developer as a result of the catalytic reaction, enabling pattern formation. Although the quantum yield of the acid generated by exposure is low, the deprotection reaction that modifies the solubility occurs many times over and the effective quantum yield of the reaction therefore increases, thus accounting for the higher sensitivity achieved in chemically amplified photoresists [13].

It follows from deprotection reaction in this way that chemically amplified photoresists are characterised by a very large change in polarity in the exposed polymer. The change in polarity gives a large solubility differential between the exposed and unexposed areas, affording increased resolution. While conferring higher sensitivity and higher resolution, chemically amplified photoresists have given rise to new problems. One difficulty is that, if a long time elapses before post-exposure bake, a
poorly soluble surface is formed, resulting in abnormal sensitivity and pattern geometry. Again, because of heavy dependence on post-exposure baking temperature, the process is greatly affected by variability in the differences within and between wafers and among baking equipment. Since the mechanism operating in a chemically amplified photoresist entails a small quantity of acid inducing many cycles of reaction, variations in acid concentration in the exposed region greatly affect pattern geometry. To solve this problem, Ito and co-workers at IBM sought improvements by modifying the base resin and proposed a chemically amplified photoresist they called ESCAP (Environmentally Stable Chemical Amplification Positive resist) [14]. The expectation was that it would be possible to ameliorate the effect of basic contaminants entering from the environment if the resist was baked at a temperature higher than the glass transition point (Tg) of the base resin so as to anneal the film and reduce the free volume within the resist. Specifically, the resin chosen was a copolymer of p-hydroxystyrene (PHS) and tert-butyl methacrylate of high glass transition point, with a protecting group (t-butyl) resisting deprotection in pre-exposure bake [15]. Improvements in both the materials and the process were thus made. Practical application of chemically amplified photoresists has been achieved by holding basic components at an extremely low concentration; thus, the air in the clean room is passed through a chemical filter as a means of preventing ingress of basic components from outside.

2.5 Chemical amplification type photoresists for ArF excimer laser lithography

To provide greater resolution, the development of lithographic technology shifted away from the KrF excimer laser (248 nm) to the ArF excimer laser (193 nm). As already noted, with every change in exposure wavelength, new resist materials (base resin and sensitizer) have been developed to match the wavelength. The particular task presented by ArF photoresist was to combine high resolution with ample dry etching resistance as a resist film. As shown in Figure 2, resins containing benzene rings such as the etching-resistant PHS have very strong absorption at the 193 nm wavelength of ArF lithography. This absorption is so strong that virtually all 193 nm light is absorbed within several tens of nm from the resist film surface. A new base resin therefore had to be developed and a resin with an alicyclic skeleton, free from benzene rings, was proposed. Initially, the three types of base resin in Figure 8 were eagerly investigated. The candidate systems comprised (1) a (meth)acrylate ester polymer with an alicyclic structure in the side chain, (2) an alternating copolymer of cyclo-olefin and maleic anhydride, (3) a polycycloolefin, i.e. a system with an alicyclic structure in the main chain.

System (2), the alternating copolymer of cyclo-olefin and maleic anhydride, and (3), the polycycloolefin with a main chain alicyclic structure, had the merits of good dry-etching resistance but eluded practical application for the following reasons. The alternating copolymer of cyclo-olefin and maleic anhydride was inevitably constrained by containing 50% of maleic anhydride in the polymer chain; and the polycycloolefin system required a special polymerization process using an organometallic catalyst. Moreover, the glass transition point (Tg) of the resins was extremely high, creating problems in film forming, and the technology failed to command centre stage. The base resin that did emerge as leader was the (meth)acrylate ester polymer with an alicyclic structure in the side chain. Specific examples of the alicyclic group are the acid-detachable adamantyl group, tricyclodecyl and norbonyl group. The alicyclic group is detached from the polymer by the acid generated in the exposed areas, forming a carboxylic acid. Since the carboxylic acid dissolves in aqueous alkali solution, the polymer functions as an ArF excimer laser positive photoresist in which the exposed areas dissolve. However, another problem arose: since the carbon-rich alicyclic

![Figure 8. Representative types of base resin for ArF photoresist](image)
group is highly hydrophobic, adhesion to the substrate deteriorates. To solve this problem, a base resin was used that had a lactone structure or alcoholic hydroxyl group introduced into the side chain, thereby achieving both high resolution and good substrate adhesion [16]. With the problems thus surmounted, practical application of ArF excimer laser lithography was realised, and combined with liquid immersion technology, led to further progress in downscaling. Mass production aimed at the 32 nm node has also been achieved by combining this technology with a double patterning process.

2.6 Photoresists for EUV

Extreme ultraviolet (EUV, 13.6 nm) lithography is seen as the most promising lithographic technology for the 32 nm node and beyond, and greatly shortens the exposure wavelength from 193 nm to 13.6 nm. Although higher resolution may be anticipated as a result, various other problems need to be solved in EUV lithography, including the mask, source and resist, the subject of much debate at academic meetings.

Light absorption by the photoresist base resin has always been problematic in photolithography. In EUV lithography the light (13.6 nm) has a very high energy of 92 eV, and since the film is thinner due to downscaling, the transmittance of the base resin is not a problem. The PHS polymer and polymethacrylate systems nurtured for the KrF lithography and ArF lithography hitherto investigated are therefore usable in terms of their light absorption. However, the quintessential element of chemical amplification photoresists is the acid catalysed reaction, and given the importance of simultaneously realising resist sensitivity, resolution and LER (line edge roughness), the expectation is that these systems cannot simply be carried across.

The reaction mechanism of EUV photoresist has been examined by Tagawa et al. and is said to be different from the reaction mechanism in existing KrF photoresist and ArF photoresist [17]. The mechanism is shown in Figure 9.

Instead of photoexcitation of the photoacid generator, the reaction in exposure of an EUV photoresist is initiated by ionization of the base resin. The mechanism continues with deprotonation from the ionised resin, counter-anion formation by reaction of the photoacid generator with secondary electrons formed in ionization of the base resin, and formation of acid by reaction between protons and counter-anions. The acid thus catalytically formed induces the deprotection reaction. Thus, atoms readily absorbing EUV light efficiently to generate secondary electrons may be anticipated to achieve higher sensitivity. As shown in Figure 10, fluorine has relatively high EUV absorption and has therefore been investigated [18] as a way of tackling the higher sensitivity requirement of the resist.

One problem specific to EUV is the need to reduce outgassing. Since gases like oxygen and nitrogen also absorb EUV light, exposure must be performed in vacuo, and residual groups from the deprotection reaction in the resist or the decomposition products of the photoacid generator could be discharged into the vacuum environment. Reduced outgassing is required because the outgas components will contaminate the mirror and mask used in the EUV exposure equipment, with adverse effects such as deterioration in resolution. The steps taken to reduce outgassing have included giving the deprotected sites and photoacid generator a bulky skeletal structure.

The task presented by an EUV photoresist is to combine sensitivity with resolution and LER (line edge roughness), and resists based on compounds other than polymers, namely low molecular weight compounds, are being investigated. A characteristic feature of low molecular weight resists is that the smaller size of the molecules allows greater monodispersion and hence solubility in developer, and should give improvements in resolution and LER. Specifically, low molecular weight resists of polynuclear phenol or cyclic polynuclear phenol structure are being widely investigated [19].

EUV lithography has matured from the research and development stage to the validation of actual device manufacture. Photoresist apart, the hardware and process areas, notably the mask and light source, also present problems but improvements are continually being made.

![Figure 9. Reaction mechanism of EUV photoresist](image)

![Figure 10. EUV absorption of elements](image)
and practical application of EU lithographic technology is eagerly awaited.

2.7 Materials for UV nanoimprint lithography (NIL)

Nanoimprint lithography is a mould processing technology for transferring ultrafine patterns of nanometre order using a curable resin sandwiched between template and substrate [20]. The technology has high throughput potential and, unlike EUV exposure, it does not require expensive, complicated equipment; it is therefore being intensively researched with a view to mass production. Nanoimprint lithography may be divided into thermal nanoimprint technology using a thermoplastic resin, and UV nanoimprint (UV-NIL) technology using a liquid photocurable resin. UV-NIL dominates in semiconductor and other fine pitch fabrication applications; the process is outlined in Figure 11.

UV-NIL resins are liquid photocurable resins, changing to solid form on exposure to light (UV); the change expresses the growth in molecular weight in polymerization of a monomer initiated by photopolymerization initiator. A number of cure systems have been proposed but the resin system most investigated for semiconductor application is of free-radical polymerization type. The composition uses a photoradical polymerization initiator and monomers containing vinyl or (meth)acrylate groups allowing free-radical initiation. Problems that remain with UV-NIL include improvement in overlay precision and defects that arise from the need to release the pattern from the template [21].

2.8 Directed self assembly

There is as yet no strong contender for the lithographic technology capable of meeting the demands of the 16 nm node and beyond and candidates are being sought from novel technologies. Attention has focussed on directed self assembly (DSA) lithography, which promotes spontaneous association of molecules from the thermodynamic standpoint and applies this to patterning. In particular, techniques using block copolymer or polymer blend materials hold the potential to realise fine-pitch patterning and are attracting much research. Figure 12 summarises the characteristics of each process.

The special feature of block copolymer lithography is its use of microphase separated domains as the lithographic template; the size and periodicity of the microphase separated domains is determined solely by the length of the block copolymer molecules. Hence, the geometry of the microphase separated domain depends heavily on the molecular weight of the copolymer, the chemical properties (polarity) of the block chains, and the respective volumes of the block chains. Typically, the block copolymer comprises polystyrene and poly(methyl methacrylate) blocks. The special feature of polymer blend lithography, on the other hand, is the concept of utilising the phase separability of a mixture of two or

Figure 11. UV-NIL process

<table>
<thead>
<tr>
<th>1. Phase-separated polymer domains</th>
<th>Block copolymer</th>
<th>Polymer blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Intrinsic dimension and pre-determined morphology</td>
<td>No specific dimension, morphology, or periodicity</td>
<td></td>
</tr>
<tr>
<td>2. Phase separation in pre-pattern</td>
<td>Block copolymer keeps intrinsic periodicity and morphology</td>
<td>Sidewall image transfer</td>
</tr>
<tr>
<td>- Specialty polymers</td>
<td>Morphology and dimension are determined by pre-pattern and blend composition</td>
<td></td>
</tr>
<tr>
<td>- Limited # of Si-based block copolymers</td>
<td>Huge material selection</td>
<td></td>
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<tr>
<td>- Difficult to perform wet development</td>
<td>Wet- or dry-etching can be applied to selectively remove one component</td>
<td></td>
</tr>
<tr>
<td>- Need ultra-high molecular weight to achieve fine features</td>
<td>Can apply to large dimensions</td>
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Figure 12. Characteristics of block copolymer and polymer blend lithographic materials
more homopolymers for fine pitch patterning. In the case of a block copolymer, the individual polymer chains are chemically combined, and after phase separation to form the pattern, a dry etching process is needed to make use of the difference in resistance to dry etching. In the case of polymer blend lithography, the two polymer chains are not chemically combined and the process therefore has the special feature that a dry etching process is not always necessary. However, some ingenuity is called for in choosing the polymer type, since in the context of phase separability a blend is inferior to block copolymer, which has the capability of imparting regular phase separation structure in the form of lamellae, cylinders, etc. As a lithographic technology for the 16 nm node and beyond, DSA still has far to go before practical implementation but is nonetheless of interest as a future processing technology.

3. CONCLUSIONS
The lithography underpinning higher level large-scale integration and downscaling of semiconductor integrated circuits currently allows the mass production of 32 nm node devices exploiting ArF immersion lithographic technology and double patterning. This could not have been achieved without developing the polymer materials central to semiconductor photoresists. Further advances in polymer technology hold the key to all the lithographic technologies of the future, namely EUV lithography, nano imprint technology, and directed self assembly, and developments are keenly awaited.

REFERENCES