Progress in Materials Development for 157nm Photolithography: Photoresists and Pellicles

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ABSTRACT

Substantial progress has been made in developing novel fluoropolymer materials for 157nm lithography. Materials with sufficient transparency at 157 nm to enable both thick single layer resists and high transmission pellicle membranes have been demonstrated. We have shown that tetrafluoroethylene (TFE)-containing 157 nm photoresist binder resins can be made that are sufficiently transparent to be used at film thickness greater than 200nm, have good photosensitivity, exhibit low outgassing upon exposure, are compatible with aqueous base development, and have etch rates comparable to PHOST resins. Optical absorbance on the order of 1.5/µm @ 157 nm should be possible for photoresists. We have now demonstrated sub-100nm 1:1 imaging in thick TFE-containing photoresists which have optical absorbance coefficients of 1.75/mm and thickness greater than 200nm. In addition, features as small as 50 nm have been imaged in a 168 nm thick film of TFE containing photoresist. Further improvements in optical transparency and high resolution imaging are anticipated utilizing fluoropolymers, and in particular TFE-based resins. In addition, a number of families of fluoropolymers have been developed which meet the transparent guidelines for pellicles. Some of these materials have now been optimized to allow unsupported membrane formation and 95% transmission, even though lifetime continues as an issue. Significant progress has been made toward 157nm lithography a realistic industry option in the context of the ITRS roadmap.

INTRODUCTION

Moore’s Law postulates that the density of transistors on integrated circuit chips will double every 18 months. This is partially due to lithographers’ continuing ability to reduce the wavelength of light used in each new optical lithography generation, from g-line (436nm) to i-line (365nm), and now to 157nm light. For the materials designer, each new lithographic wavelength has demanded the development and optimisation of new materials for use as photoresists, photoresists and membranes, and lenses and optical coatings. At the same time the optical properties and behaviour of materials change with wavelength, and the performance requirements for the different applications become more stringent and numerous.

The International Technology Roadmap For Semiconductors (ITRS Roadmap) first listed 157nm lithography as a technology option in 1998, even though preliminary work on the feasibility of 157nm as a lithography wavelength was done earlier, ref [1]. At first 157nm lithography was viewed as a candidate for the 100nm and 70nm semiconductor feature size nodes in 2004 and 2007; an interim update to the ITRS roadmap now views it as a candidate for the 90 and 65nm nodes in those same years, ref [2]. 157nm lithography is viewed as the last traditionally “optical” lithography, in which transmissive optics are used in the lithographic stepper/scanner and the photomasks are of the conventional transmissive type. However, this is the first lithographic wavelength in which the stepper must be nitrogen-purged due to the strong optical absorption of the oxygen and water vapour components of air at 157nm. The 157nm photon energy is 7.87eV, and as a result the fundamental photochemistry of materials can be very different from that seen at the longer, lower photon energy lithography wavelengths used previously.

Successful development of 157nm lithography requires the development of reliable F2 excimer lasers, CaF2 optical materials for lenses and optics, new fabrication techniques for lens manufacturing, and techniques to assure a nitrogen purged environment in the stepper, eliminating oxygen, moisture, hydrocarbons and other possible deleterious contaminants. In addition, photomask materials, such as attenuating phase shift materials, ref [3], and photoresist substrates with sufficient transparency at 157nm, must be developed (as have modified fused silica materials), ref [4].

The two 157nm materials development challenges on which we will focus in this article involve novel fluoropolymers for use as photoresists, ref [5] (for photolithographic imaging) and soft pellicles, ref [6] (for contamination control of photomasks).

SINGLE LAYER FLUOROPOLYMER PHOTORESISTS

The primary challenge in the design of chemically-amplified resist resins for use at 157nm is to find materials which simultaneously possess the following four properties: good optical transparency, good photosensitivity for latent image formation, suitable solubility in aqueous base after deprotection, and good etch resistance, ref [7]. These requirements have led to the development of various resist strategies and materials families.
Thick single layer resists are the most desirable approach since they are the simplest and therefore most robust from a process point of view. But when optical absorbance of the resist reduces the acceptable imaging film thickness below a value which provides enough etch resistance, alternate approaches become attractive. For example, in thin layer imaging (TLI) the resist film thickness is dramatically reduced to permit reasonable image formation, but the issue of high defect densities in these thin layers and associated yield losses has strongly discouraged widespread acceptance of TLI in production. Another approach is the use of bi-layer or top surface imaging resists, ref [8]. An example is the silylation resists, ref [9], in which a thin top layer is used for image formation through a silylation process. This pattern is then transferred through the thickness of the resist film by a dry development step. Bi-layer resists require a larger number of process steps than single layer resists and therefore typically have lower device yields. In addition, for the silylation resists the presence of significant line edge roughness in the resist layer has been an issue. A combination of TLI and bi-layer processing is used in a hard mask approach, where a single layer resist is used on top of a thin, hard mask film such as silicon oxide or silicon nitride, and an oxide or nitride etch is used to transfer the resist pattern into the hard mask. Once this is accomplished, the hard mask material serves to supply the patterned etch resistant layer for the subsequent process step.

For a single layer resist, the optical transparency requirement restricts the permissible film thickness according to the optical absorbance of the material, ref [10]. Optical modeling has shown more vertical sidewalls for a photoresist imaging layer with an optical density (O.D = Thickness*Abs/um) less than 0.4 and this corresponds to an optical absorbance (base 10) below 2.0/µm, in which a thin top layer is used for image formation through a silylation process. This pattern is then transferred through the thickness of the resist film by a dry development step. Bi-layer resists require a larger number of process steps than single layer resists and therefore typically have lower device yields. In addition, for the silylation resists the presence of significant line edge roughness in the resist layer has been an issue. A combination of TLI and bi-layer processing is used in a hard mask approach, where a single layer resist is used on top of a thin, hard mask film such as silicon oxide or silicon nitride, and an oxide or nitride etch is used to transfer the resist pattern into the hard mask. Once this is accomplished, the hard mask material serves to supply the patterned etch resistant layer for the subsequent process step.

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**Fluorinated Acidic Groups for Aqueous Base Development**

The ability to balance multiple, at times conflicting, properties is essential to materials design. One tradeoff in photoresists is between optical transparency at 157nm and aqueous base solubility. The use of fluorinated resins was, and still is, perceived as a serious impediment to achieving proper dissolution characteristics due to the well-known hydrophobicity of many fluoropolymers (for example, Teflon®). Nevertheless, we have found that it is possible to achieve reasonably good dissolution characteristics using resists which are highly fluorinated through the judicious incorporation of protected and unprotected acid groups.

Conventional acidic groups, such as phenols and carboxylic acids that are ubiquitous in 248 and 193nm resists, are too absorbing at 157nm to be used in sufficiently high quantities to solubilise binder resins in aqueous base developers. However, in 1992 Pryzbilla and co-workers at Hoechst reported on the use of the hexafluoroisopropanol group for polystyrene-based 248nm resists. They found the fluoroalcohol group could be blocked with the t-butoxycarbonyl protecting group for use in chemically amplified systems, ref [11]. In 1997, Ito and coworkers at IBM reported on copolymers of SO3 with norbornenes functionalised with the hexafluoroisopropanol group as 193nm photoresist binders, ref [12]. The hexafluoroisopropanol group appears to be far less absorbing at 157nm than other acidic functionalities, ref [13], and is a key component in several of the new 157nm photoresist binders currently undergoing development.

**Fluorinated Resins as 157nm Photoresist Binders**

Early in the development of 157nm lithography the suggestion was made to turn to fluoropolymers as the resist resins for single layer resists (SLR), since some were found to be surprisingly transparent at 157nm, ref [10]. One of our goals has been to identify fluorinated polymer backbones that have good transparency at 157nm, good imaging performance, acceptable plasma etch resistance, high glass transition temperature (Tg), and compatibility with conventional 0.26 N tetramethyloxonium hydroxide developers.

As an example of one of our approaches, let’s consider copolymers of tetrafluoroethylene (TFE) with multicyclic olefins. The 1:1 copolymer of norbornene (NB) and TFE, prepared by free-radical copolymerisation, is just such a material. NB/TFE copolymers have excellent transparency at 157nm (Abs = 1.0/µm), high glass transition temperatures (Tg = 150°C), can be synthesised with molecular weights appropriate for photoresist binders (Mn = 3,000), and have etch rates comparable to that of novolak, ref [13].

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\begin{align*}
\text{CF}_3 \quad \text{CF}_2 \quad \text{CF} &\quad \text{CF}_2 \quad \text{CF}_3 \\
\end{align*}
\]

Of course, NB/TFE by itself does not contain the acidic functional groups necessary for aqueous base development and adhesion to silicon. As noted above, the hexafluoroisopropanol group is both acidic (pKa ~ 9, comparable to phenol), and fairly transparent at 157nm, refs [13] & [14]. By incorporating this group, as well as some other functional groups, into TFE copolymers of multicyclic olefins, we have been able to synthesise materials that can be developed using conventional aqueous base developers, while still maintaining good transparency at 157 nm (Abs @ 157nm ≤ 2.5/µm).

There are other approaches to etch resistant, aqueous-base soluble materials that do not incorporate fluorene directly into the polymer backbone. For example, both we and the UT-Austin group have been working with vinyl addition copolymers of norbornene-fluoroalcohols, refs [13] & [14]. An example of a copolymer binder that has been reported recently by workers at UT-Austin and Clariant is shown below. Vinyl addition copolymers of this type have absorption coefficients of approximately 3/µm, depending on how much ester group they contain. This can be compared to 6.1/µm for unfunctionalised polynorbornene, ref [10]. Thus, attachment of hexafluoroisopropanol groups to the polynorbornene backbone dramatically reduces 157nm absorbance.
Optimum imaging performance at 157nm is obtained when these materials are formulated with low molecular weight additives; e.g. a co-oligomer of carbon monoxide and the tert-butyl ester of 5-norbornene-2-carboxylic acid, ref [15].

Polystyrene is another etch resistant backbone that can be rendered both less absorbing at 157nm and soluble in aqueous base by the addition of fluoroalcohol groups. For example, workers at IBM and MIT-Lincoln Laboratory have recently described copolymers of the type shown below; ref [16]. These ESCAP analogs have absorption coefficients at 157nm in the range of 3.5-4.0 /µm, and have been imaged at 157nm in films as thick as 125nm. Again, the fluoroalcohol group greatly reduces absorbance: the 157nm absorbance of polystyrene itself is 6.2/µm, ref [1] & [10]. The incorporation of tert-butyl 2-(trifluoromethyl)acrylate in place of tert-butyl methacrylate further reduces 157nm absorbance. The transparency benefits of incorporating (trifluoromethyl)acrylates into polymer backbones has also been noted by the UT-Austin group, ref [13].

Workers at Cornell have designed and synthesized 157nm photoresists resins based on copolymers of poly(2-trifluoromethyl vinyl alcohol). As in the systems described above, the fluoroalcohol group in these polymer resins imparts acidity as well as improvement in transparency, ref [17].

Optical Transparency

As noted above, fluorine can be incorporated into both the polymer backbone and into acidic side chains (e.g. as fluoroalcohol groups). There is a clear advantage in terms of optical transparency in incorporating fluorine into both parts of the resin. In Figure 1 we show the optical absorbance of a vinyl addition norbornene-fluoroalcohol homopolymer (NBR/NBR') which has an optical absorbance (base 10) of 2.0/µm at 157nm. The optical absorbance of a comparable TFE copolymer (TFE/NBR/NBR') is reduced to 0.98/µm.

Spin Coating, Film Formation and Adhesion

The film forming and spin coating properties of a photoresist are essential to accurate imaging, CD control, and defect reduction. Therefore the base resins and formulated resists must be compatible with conventional spinning solvents, have mutual miscibility with formulation additives such as photoacid generators (PAGs) and dissolution inhibitors (DIs) and have excellent wetting and leveling properties. The TFE copolymers described above meet these requirements since they are readily soluble in common spinning solvents (e.g., 2-heptanone or PGMEA) and exhibit good wetting behaviour. As a demonstration of this, film uniformity measurements made on hand dispensed photoresist films spin coated onto 8inch HMDS primed Silicon Wafers show typical thickness uniformities of +/- 0.5nm. In addition, no coating defects are visible when films are viewed under monochromatic light.

Etch Resistance

Another essential materials property for 157nm single layer photoresists is etch resistance since, as discussed above, these will be used at thicknesses significantly less than for 193 or 248nm resists. Thus the ability of a 200nm thick resist to withstand etching requires etch resistance comparable to or greater than poly-parahydroxy styrenic (PHS). In Table 1 we show etch rates relative to PHS-based resist for several fluorinated resins of both

**Table 1. Etch rates, relative to a commercial PHS-based resist, of several VA and TFE resins**

<table>
<thead>
<tr>
<th>Resin</th>
<th>Polysilicon Etch Rate a</th>
<th>Silicon Oxide Etch Rate b</th>
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<tbody>
<tr>
<td>PHS Resist control</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>VA Copolymers</td>
<td>1.3</td>
<td>1.2</td>
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<td></td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>TFE Copolymers</td>
<td>0.9</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>1.1</td>
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* Cl2/HBr chemistry on a TCP etcher
* C4F8 chemistry on a Tel Oxide etcher
* Commercial 248 nm resist based upon poly-parahydroxy styrene

Figure 1
Optical absorbance of base resin for 157nm single layer photoresists, comparing TFE containing and vinyl addition resins.
the VA and TFE copolymers, under both poly-Si and oxide etch conditions. The data demonstrate that etch rates comparable to PHS are achievable using fluoropolymers which also have good transparency at 157nm. Finally, the TFE copolymers have quite good etch rates, indicating that incorporation of significant quantities of TFE in the polymer backbone does not cause the etch rate to increase.

Outgassing
Outgassing of organic or inorganic compounds from 157nm photoresists upon exposure is a critically important property that must be controlled due to the potential for contamination of the stepper optics and degradation of the steppers’ imaging performance, refs. [18] & [19]. The resists we are developing exhibit low outgassing rates upon 157nm exposure, which were comparable to, or at the lower end of the range of, standard 248 nm resists exposed to 157nm radiation, ref [20]. Most of the photofragments detected by mass spectroscopy were related to either PAGs or DIs. There was no significant outgassing associated with the components of the fluorinated base resins (such as TFE) and any fluorinated fragments can be cleaned from the optical elements using laser or lamp cleaning procedures.

Photolithographic Imaging Performance
We have imaged a number of formulated resists using the 157nm Exitech/Tropel stepper at International Sematech. Here we will describe the results for copolymer resins of TFE/NB with functionalised norbornene-type monomers and other monomers (e.g. monomers which include protected acidic groups). All imaging presented here was performed on bare silicon wafers, primed with HMDS. An alternating phase shift mask (altPSM) was used in each case. Note that the use of an altPSM, results in loops at the ends of adjacent printed lines. The resists have been imaged at either the first Rmin (comparable to the Emax) which typically arises at ~160nm thickness or at the second Rmin which arises at ~205nm film thickness. For each resist the optical constants are determined using a J. A. Woollam VUV-Vase Spectroscopic Ellipsometer. These optical constants are used to determine the reflectance swing curve, and the desired film thicknesses. The 157nm optical absorbance of the resists with film thicknesses of ~205nm was 2.9/µm while the resist imaged at 156nm thickness had an absorbance of 2.3/µm. We used a top down SEM to optimise the lithographic imaging parameters such as focus and exposure.

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Figure 2
Focus exposure matrix for 100nm features in a TFE containing fluoropolymer photoresist with a film thickness of 205nm on HMDS primed silicon, using SEMATECH’s Exitech/Tropel 157nm stepper with an alternating phase shift mask and a partial coherence of 0.3sigma. The exposure doses are calculated by dividing the reported exposure dose by a factor of 3.4 to compensate for the 0.3sigma aperture.

Figure 3
Isolated to dense features of nominal 90 and 100nm feature size in a TFE containing fluoropolymer photoresist with a film thickness of 205nm on HMDS primed silicon at one focus and exposure, using SEMATECH’s Exitech/Tropel 157nm stepper with an alternating phase shift mask and a partial coherence sigma of 0.3. Features sizes, measured using the box method on the top down scanning electron microscope, are listed below each image.
Figure 2 shows a portion of a focus exposure matrix created in a 205nm thick TFE-based resist having an absorbance of 2.9/\(\text{nm}\). From top down SEM images of 100 nm 1:1 dense lines, we find a 0.3nm focus latitude. Examining exposure effects in the same region of the test pattern we find proper imaging from 15.0mJ to 16.2mJ representing an exposure latitude of 8%. These are conservative estimates since a thorough cross section analysis was not done.

The feature sizing bias that results from going from isolated to dense features, when evaluated at the single focus and exposure value that results in proper sizing of isolated features, is another useful imaging performance evaluation. In Figure 3 we show the sizing of 90nm and 100nm features, that range from isolated to 1:1 dense. The apparent reduction in the line height in the 1:1 dense image arises from a mask issue, and is not apparent at positions far away from the line ends and the loops. Here we see that for both 100 and 90nm features, there is an iso/dense bias that, for a single focus/exposure setting, produces dense features smaller than nominal size. This effect has been seen in other resists and can be varied by changes in PAB and PEB processing, ref [21]. For both 100 and 90nm features, the iso/dense bias, as determined from top down SEM images, showed isolated features that are larger than the dense features, with a CD range of 27nm and this corresponds to an iso/dense bias of -27nm.

The ability to create properly sized features of differing sizes at a best focus and exposure value is also important. For a 205nm thick TFE containing photoresist film, we can size 70 to 180nm isolated features at one focus and exposure. Figure 4 shows properly sized features ranging from 70 to 180nm created at a single focus/exposure setting, in a 205nm thick TFE containing photoresist film. Only the 60nm isolated features print oversized as determined by top down SEM.

Cross sections taken on two different TFE containing resists are shown in Figure 5. Here the 90nm features are from a 205nm thick resist, with an optical absorbance of 2.9/\(\mu\text{m}\). We can see that the line shapes have a sloping side wall. Even though the lines have flat tops, the width of the lines measured at the base is oversized. The 100nm features in the figure are for a resist with an optical absorbance of 2.3/\(\mu\text{m}\) and a film thickness of 156nm. The lower O.D. results in sizing closer to the 100nm target feature size. Also, the wall angle of the resist lines is closer to 90 degrees than for the high O.D. film discussed earlier. These profiles are far from ideal, but these images do demonstrate the imaging potential of the polymer platform.

Line edge roughness (LER) is also a critical requirement in the imaging performance of resists for 157nm lithography. In Figure 6 we show a top down SEM image of 100nm 1:1 dense lines and spaces for a resist that shows little apparent line edge roughness. To date we have not quantified the LER.

Quite recently we have further improved the properties of our TFE-based fluoropolymer resists. We have now demonstrated sub-100nm imaging with resists which have an optical absorbance of 2.3/\(\mu\text{m}\) and a film thickness of 156nm. The lower O.D. results in sizing closer to the 100nm target feature size. Also, the wall angle of the resist lines is closer to 90 degrees than for the high O.D. film discussed earlier. These profiles are far from ideal, but these images demonstrate the imaging potential of the polymer platform.

Cross sections taken of nominal 90 and 100nm lines in TFE containing fluoropolymer photoresist on HMDS primed silicon using SEMATECH’s Exitech/Tropel 157nm stepper with an alternating phase shift mask and a partial coherence sigma of 0.3. Reported features sizes were measured at the base of the lines.
The optical absorbance of the resist is 1.75/µm and the sizing dose is 7 mJ/cm².

Figure 7
80 nm isolated, 1:5 and 1:3 lines and spaces in a TFE containing fluoropolymer photoresist with a film thickness of 211nm on HMDS primed silicon using SEMATECH’s Exitech/Tropel 157nm stepper with a binary phase shift mask and a partial coherence sigma of 0.7. The optical absorbance of the resist is 1.75/µm and the sizing dose is 7 mJ/cm².

Figure 8
50nm 1:3 lines and spaces in a TFE containing fluoropolymer photoresist with a film thickness of 164nm on HMDS primed silicon using SEMATECH’s Exitech/Tropel 157nm stepper with an alternating phase shift mask and a partial coherence sigma of 0.3. The optical absorbance of the resist is 2.3/µm and the sizing dose is 15.3 mJ/cm².

SOFT PELLICLES
The primary challenge in the design of photomask pellicles for use at 157nm is different from that found for photoresists. For polymeric pellicles one requires much higher optical transparency, film properties that allow formation of unsupported membranes, and sufficient photo insensitivity of the material to yield long lifetimes under 157nm irradiation. Pellicles are used as contamination control devices for photomasks to keep particles out of the object plane of the stepper occupied by the photomask pattern. Current pellicles for 248 and 193nm lithography are soft fluoropolymer membranes, typically 0.8µm thick, whose interference fringes are tuned to produce transmission maxima at one or several lithographic wavelengths. This tuned etalon design assures that the pellicle has minimal impact on the optical imaging system of the stepper. In addition to transparency, the pellicle material must have the necessary film forming properties to produce unsupported, large area membranes with good mechanical strength to survive standard cleaning processes. The pellicle membrane must also have sufficient radiation durability, i.e., be photoinensitive, so that it doesn’t degrade under prolonged irradiation at the lithographic wavelength. Degradation can be the result of outgassing that causes membrane thinning or it can be increased absorption causing a drop in transmission. Initially, no polymeric materials were known that could be used to make a “soft” polymeric pellicle with sufficient transparency at 157nm. An alternative “hard” pellicle of 157nm transparent modified fused silica of 500 to 800µm thickness was proposed. Although materials for a “hard” pellicle can be found with sufficient transparency at 157nm, the increased thickness and the uniformity requirements impose substantial design complications and restrictions on the stepper optics.

Initial results from MIT Lincoln Labs demonstrated that the commercial fluoropolymers used for pellicles at 248nm and 193nm wavelengths, such as Teflon AF® and Cytop®, have no mechanical integrity and rapidly burst under irradiation with 157nm light. Therefore we have undertaken an extensive program to screen for, and develop, novel fluoropolymer candidates which have the required combination of optical properties, film-formation properties, and radiation durability (both mechanical and photochemical) to produce 157nm pellicles.

Optical Transparency
The optical absorbance/µm of two commercial amorphous fluoropolymers, TeflonAF® and Cytop®, used to make pellicles, is shown in Figure 9. The 157nm transmission of a pellicle membrane of TeflonAF® would be ~45% while Cytop® would have a 157nm transmission of ~2.5%. Studies show that these fluoropolymers become perforated rapidly under 157nm laser irradiation, with failure typically occurring for an exposure dose on the order of 1J. For commercial TeflonAF®, we estimate that the pellicle lifetime for a 10% drop in 157nm transmission would be on the order of only 0.001J.

Materials design and development of ultra transparent fluoropolymers suitable for 157nm soft pellicle applications has produced a number of promising candidate materials with absorbances (shown in Figure 10) below 0.03/µm which would enable pellicle transmissions above >95%.

Polymer and Pellicle Properties
The next step is optimisation of the polymer’s molecular weight and the spinning solution viscosity required for membrane formation. Other pellicle physical parameters such as thickness (which produces the tuned interference fringes in the optical behavior of the membrane), degree of surface roughness, and thickness non-uniformity must also be optimised. Careful consideration and
control of the end use and environmental aspects of the 157nm pellicle application are also important, ref [19]. For example, adsorbed oxygen, water, and hydrocarbons can reduce the 157nm transmission. The transmission of a TAFx3P pellicle with 95% transmission near 157nm is shown in Figure 11.

**Radiation Durability & Lifetime**

Upon irradiation, these 157nm pellicle polymers undergo photochemical darkening which reduces the 157nm transmission of the material. Measurement of the photochemical darkening rate allows the estimation of useful pellicle lifetime defined as the dose required for a 10% drop in 157nm transmission. Increasing the 157nm lifetime of fluoropolymers involves simultaneous optimisation of the materials, the pellicles, and the end use application. Similar optimisation was essential to achieving the radiation durability lifetimes required for pellicles successfully developed for use with KrF (248nm) and ArF (193nm) lithography.

**CONCLUSIONS**

Substantial progress has been made in developing novel fluoropolymer materials for 157nm lithography. Just a few years ago, the ITRS roadmap showed no known solutions to the requirements for resist and pellicle materials. Now, materials with sufficient transparency at 157nm to enable thick single layer resists and high transmission pellicle membranes have been demonstrated and formulated. 157nm photoresists with optical absorbance on the order of 1.3/µm should be possible. We have shown that TFE-containing 157nm photoresists can be made which are sufficiently transparent to be used at film thicknesses of 200nm, have good photosensitivity, exhibit low outgassing upon exposure, that are compatible with aqueous base development and have etch resistances comparable to PHOST resins. Imaging of 90 and 100nm 1:1 dense lines and spaces with reasonable focus and exposure latitude has been demonstrated in 205nm thick films of these resists.

Quite recently we have further improved the properties of our TFE-based fluoropolymer resists. We have now demonstrated sub-100nm imaging in thick resists (thickness > 200nm) which have optical absorbance coefficients of 1.75/µm, the best performance for such a low optical absorbance photoresist reported to date. In addition, we have imaged features as small as 50nm in a film of thickness 168nm, slightly greater than a 1:3 aspect ratio. We are greatly encouraged by these recent results and believe that further improvements in optical transparency and high resolution imaging will be achieved using fluoropolymer, and in particular TFE-based, resins.

For fluoropolymer pellicles, the transparency requirements are more stringent, requiring optical absorbances below 0.3/µm. We have now developed a number of families of fluoropolymers which meet these guidelines. Some of these materials have now been optimised to allow unsupported membrane formation. Pellicles with 95% transmission have been produced. Reduction of photochemical darkening during use is the current focus of the effort to extend the lifetime of the pellicles in the end use application. The progress in materials design and development of these novel materials for 157nm lithography demonstrates the flexibility of fluoropolymers to achieve an impressive array of what at times appear to be dissimilar properties. This progress represents an important step in bringing 157nm lithography to market on time.
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