A Review of Material Issues in Immersion Lithography

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ABSTRACT

The emergence of immersion lithography as the next lithographic extension to keep pace with Moore's law has resulted in new considerations regarding resist issues. In traditional dry lithography, the resist stack is isolated, only reacting with photons and the ambient environment during exposure. The diffusion of materials is limited to the diffusion lengths as prescribed by baking temperatures, specifically the post exposure bake. Liquid Immersion Lithography, a wet lithography process, introduces a fluid medium between the lens and resist stack to increase the depth of focus, effective NA, and ultimate resolution of the 193nm lithography toolset. The optical coupling of the immersion liquid with the resist stack has challenged the lithography community to understand the physical dynamics of this resist/water interaction and reveal any significant challenges early in the development. Issues such as water penetration into the resist matrix and the leaching of the photoacid generators and base quenchers into the water are the fundamental interactions. The extents of these interactions and the effects on resist performance have been the subject of many studies. The challenge to resist chemists is to select material systems to meet current requirements while considering the forecast of the technology roadmap as critical dimensions steadily decrease to the 65nm and 45nm nodes.

1. INTRODUCTION

Immersion lithography at 193nm is currently being investigated as the next lithographic step to decrease resolution as the semiconductor industry keeps pace with Moore's law. Resolution, R, as shown in equation 1, is proportional to wavelength and inversely proportional to the numerical aperture (NA) of the optical system. Improvements in resolution have traditionally been achieved through steady reductions in wavelength; from 436nm(g-line Hg), 364nm(i-line Hg), and 248nm(KrF excimer), to 193nm(ArF excimer) which is currently utilized in the industry. Attempts to further reduce the wavelength to 157nm(F2 excimer) has been met with many challenges and is currently not considered feasible to be widely implemented in a production environment.

$$R = k_1 \frac{\lambda}{n \sin\theta} = k_1 \frac{\lambda}{NA} \quad (1)$$

Immersion lithography is an optical enhancement technique that increases the effective NA of the optical system. The optical enhancement is achieved by placing a fluid between the final element of the projection lens and the resist stack on the surface of the wafer. For a system utilizing water as the immersion fluid (n=1.437 @ 193nm), an optical system producing 65nm L/S is potentially capable of fabricating 45nm L/S if the materials permit.

Building from the current platform of "dry" lithography materials at 193nm, resist chemists examine the material compatibility with immersion lithography. The interactions of the immersion fluid with the resist matrix present new considerations to the formulation of an ideal immersion resist. Interactions include the penetration of the immersion fluid into the resist matrix, and the enhanced diffusion and removal of resist components into the fluid. Understanding the fluid-resist interactions is fundamental to the engineering of materials that can leverage this new class of immersion lithography systems with decreasing feature size.

2. **LITHOGRAPHIC MATERIALS**

Chemically amplified resists (CA resists or CARs) utilized at 193nm are formulated with three primary components; the polymer resin, photoacid generator, and base quencher. Additional components, such as casting solvents and dissolution inhibitors, offer additional functionalities as needed in a given formulation.

The following is a summary of the various components of a resist formulation with functional descriptions. The materials referenced in the reviewed papers are listed, including acronym and proper name.

Polymer Resins

The components of the polymer resin, generally a ter-polymer (3 components) or tetra-polymer (4 components), are the backbone of the resist matrix.

MMA – methyl methacrylate
TBMA – t-butyl methacrylate
MAA – methacrylic acid
MAdMA – 2-methyl-2-adamantanol methacrylate (for dry etch resistance)
GBLMA – gamma butyrolactone
HadA –
MLMA – mevalonic lactone methacrylate (for wetability and adhesion)
COMA – cycloolefine-maleic anhydride
- BNC - t-butyl-5-norbornene-2-carboxylate
- MA - maleic anhydride

HNC – Hydroxyethyl-5-norbomene-2-carboxylate
NC – 5-norbornene-2-carboxylic acid
VEMA – vinyl ether-maleic anhydride

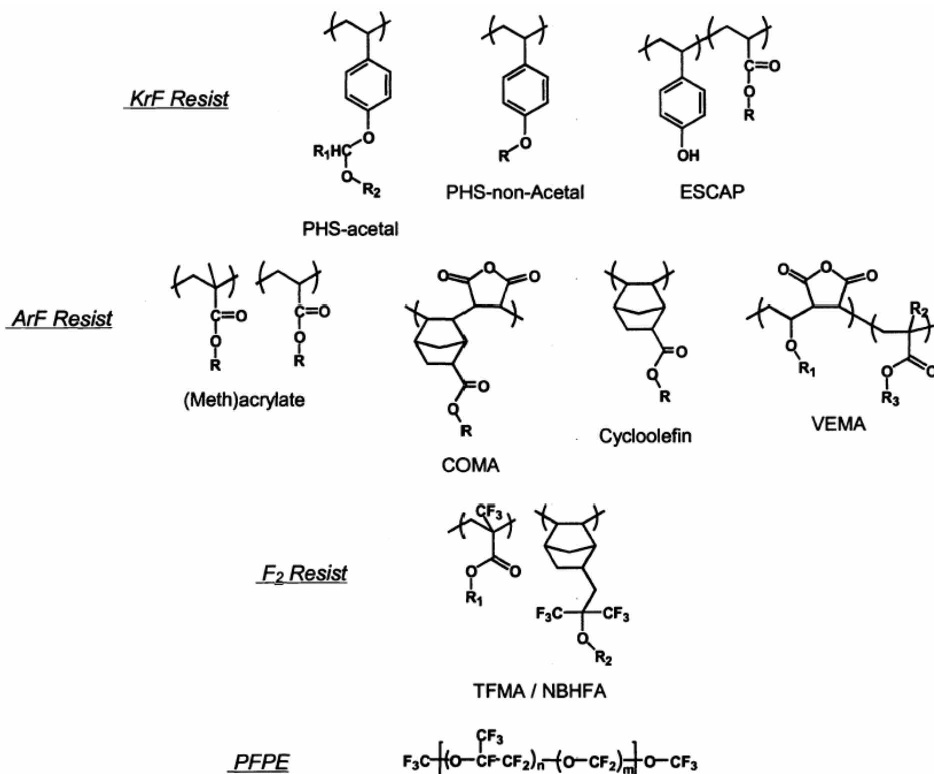

Figure 1. The components of polymer resins investigated by Kishimura. PFPE is used as the immersion fluid for the F_2 resists, while H_2O and PFPE were investigated for ArF resist formulations.[1]

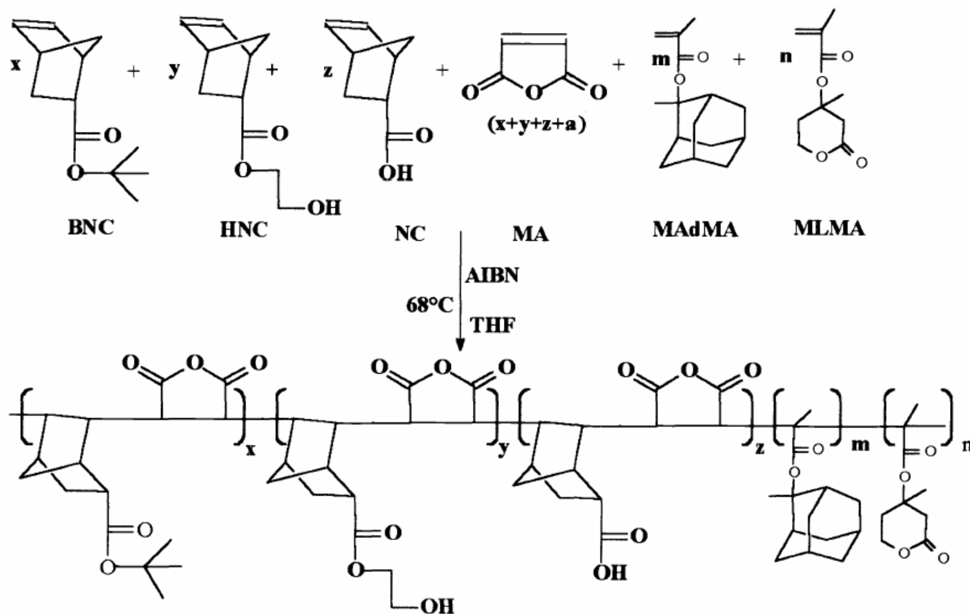

Figure 2. Structure of hybrid COMA/methacrylate copolymer (similar to Clariant T2030).[2]

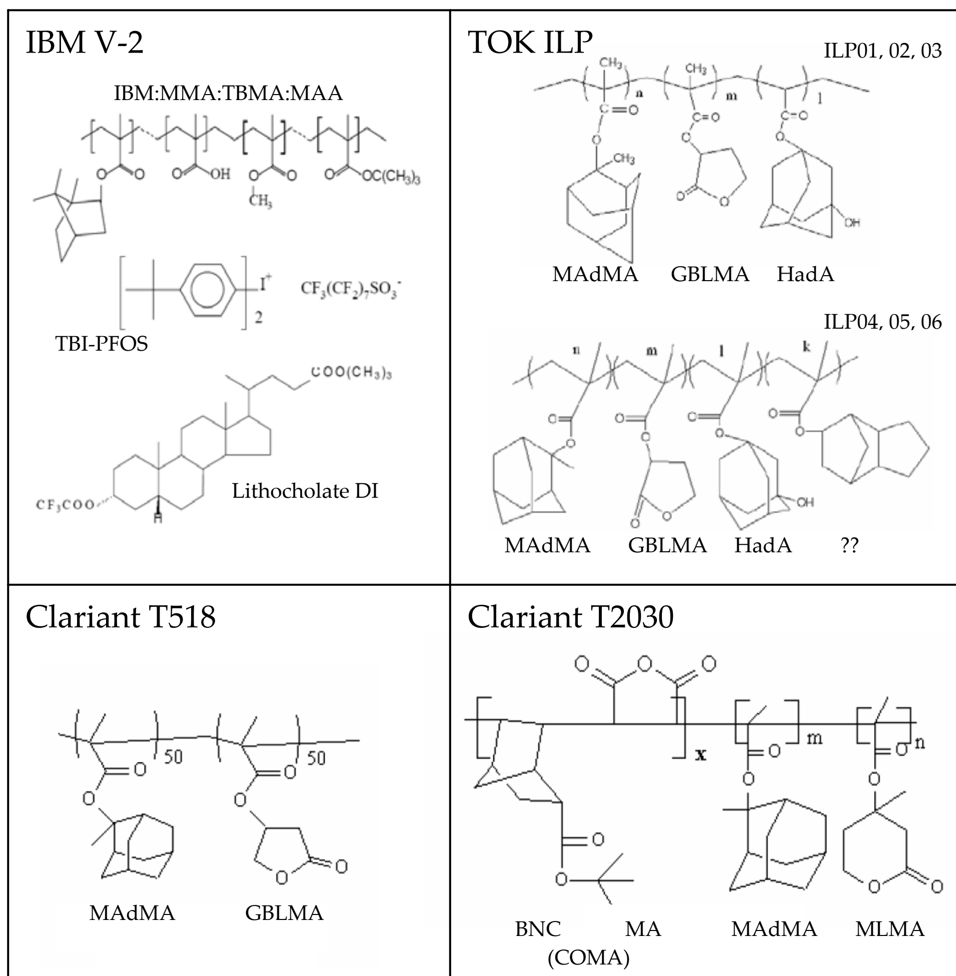

Figure 3. Resist structures investigated by Hinsberg[3], and Raub[4].

Photoacid Generators
The photoacid generators (or PAGs) react with photons, creating an acid which reacts with the polymer resin to deprotect the resin. The acid deprotection then allows the developer to dissolve the polymer chain.

<u>Iodonium Salts</u>
TBI-PFOS – *tert*-butylphenyliodonium perfluorooctanesulfonate
<u>Sulfonium Salts</u>
TPS-PFBS – triphenylsulfonium perfluorobutanesulfonate
(or TPS-Nf – triphenyl sulfonium nanoflate)
TPS-T$_f$ – triphenylsulfonium trifluoro sulfonate (or triphenyl sulfonium triflate)

Base Quenchers
The base quenchers limit the diffusion of the photogenerated acid and minimize blur.

TBAH – tetra butyl ammonium hydroxide
TEA – triethanolamine
TPA – tripentylamine
TDDA – tri-n-dodecylamine (aka trioctylamine?)

Casting Solvents
The casting solvent functions to dissolve the polymer resins and act as a carrier to uniformly distribute the material during typical spin-coating processes, then predominantly evaporating away during the post-application bake (or PAB).

PGMEA – propylene glycol methyl ether acetate
EL – ethyl lactate
MAK – methyl amyl ketone
PGME – propylene glycol monomethyl ether

Dissolution Inhibitor
Lithocholate DI – dissolution inhibitor

Developer
The developer dissolves the deprotected polymer chains in the resist matrix.

TMAH – tetramethyl ammonium hydroxide (0.26N industry standard)

3. **WATER – RESIST INTERACTIONS**

The interaction of the immersion fluid with the resist matrix is a new consideration for the resist chemist. The penetration of water into the resist has the potential to diffuse the PAG and base quencher within the matrix and leach some portion of the components into the immersion fluid.

Water Penetration
Hinsberg et al. investigated the penetration of water into the resist matrix.[3] Quartz crystal microbalance and optical reflectance techniques were used to characterize the swelling and water uptake. The resist formulations investigated by Hinsberg are compiled in Table 1.

Table 1. Resist formulations for IBM and TOK resists.[3]

<table>
<tr><th></th><th>Polymer Resins</th><th>Casting Solvent</th><th>PAG</th><th>DI</th><th>Base Quencher</th></tr>
<tr><td>IBM V-2</td><td>IBM:MMA:TBMA:MAA
(25:30:10:35)</td><td>PGMEA</td><td>TBI-PFOS
(5 parts)</td><td>Lithocholate DI
(20 parts)</td><td>TBAH
(0.2 parts)</td></tr>
<tr><td>TOK-ILP01</td><td rowspan="3">(ter-polymer)
MADMA:BLMA:HadA
(28:52:20)</td><td rowspan="3">PGMEA:EL
(60:40)</td><td rowspan="3">TPS-PFBS
(5 parts)</td><td rowspan="3"></td><td>TEA
(0.3 parts)</td></tr>
<tr><td>TOK-ILP02</td><td>TPA
(0.46 parts)</td></tr>
<tr><td>TOK-ILP03</td><td>TDDA
(1.05 parts)</td></tr>
</table>

For TOK ILP01 resist, the swelling of the resist is measured over a 300 second time period as shown in Figure 4a. The projection for the contact time of water in commercial tools is estimated to be less than 30 seconds. Within the first 10 seconds, a 200nm film swells by ~ 2 ppth (parts per thousand), 2.5 ppth after 30 seconds, and 4 ppth after 300 seconds. Deuterated water (D2O or heavy water) water was used to demonstrate the relatively uniform distribution of water through the TOK ILP02 photoresist. Residual components of the deuterated water are measured by Secondary Ion Mass Spectroscopy (SIMS) to determine the concentration profile as a function of depth as shown in Figure 4b.[3]

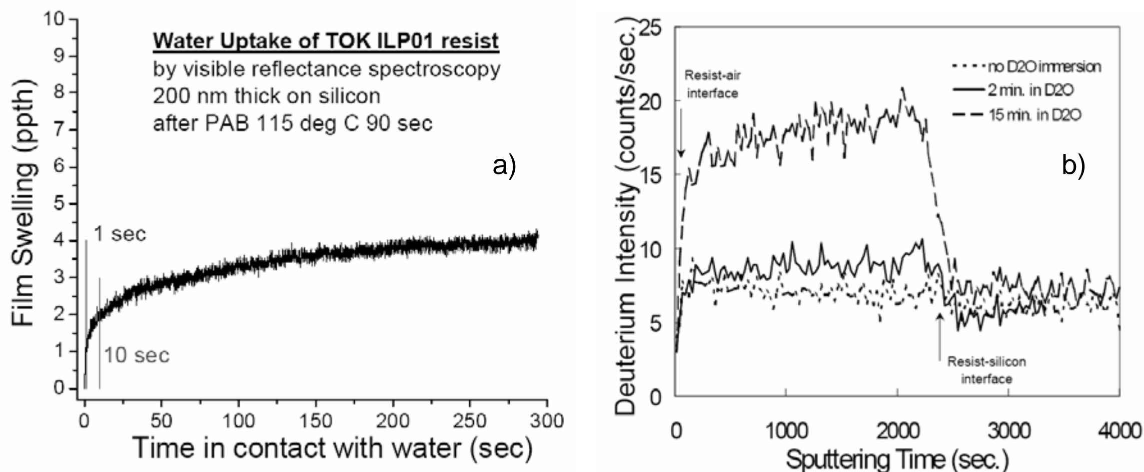

Figure 4. The interaction of water with the resist film is demonstrated by a) the swelling of resist in contact with water as measured by optical reflectance and b) the uniform penetration of deuterated water into the resist matrix as measured by SIMS analysis.[3]

Leaching – Extraction of resist components into water

Near-edge X-ray absorption fine structure spectroscopy (NEXAFS) was used to investigate the change in the film composition on the surface of the IBM V-2 resist.[3] For a 50nm film, 50% of the PAG was depleted from the top 25nm once the water made contact with the resist regardless of UV exposure. Lithocholate DI was not significantly affected by the water interaction.

Further analysis with gas/liquid chromatography and mass spectroscopy was used to detect extracted resist components in aqueous samples.[3] The results are shown in Table 2. Table 3 shows the equilibrium solubility for the various resist components and byproducts in water.

For IBM-V2 resist, water in contact with the resist for 2 minutes extracted 5-10% of the available PFBS ($C_8F_{17}SO_3^-$) available in the film, 0.1ppm for unexposed resist, 0.2 ppm with UV exposure. Lithocholate DI and TBAH were not detected regardless of exposure conditions. Similar results were yielded with the TOK resist with detection of the ($C_4F_9SO_3^-$) anion. The base components, TEA and TDDA for TOK-ILP01 and TOKILP03 respectively, were extracted and detected for the unexposed condition, but not detected for the exposed condition. The writer speculates that the base components are extracted, but interact with the photogenerated acid 'to form a nonvolatile and therefore undetected salt'.[3]

Table 2. Amounts of resist components and byproducts extracted into the water layer during contact, as determined by organic trace analysis. [3]

	Unexp	Exp	Unexp	Exp
IBM-V2	$C_8F_{17}SO_3$- *	$C_8F_{17}SO_3$- *	TBAH and DI	TBAH and DI
2 min	0.1 ppm	0.2	ND	ND
TOK-1	$C_4F_9SO_3$- *	$C_4F_9SO_3$- *	TEA	TEA
1min	0.10 ppm	0.066	0.31**	ND
15	0.070	0.088	0.22	ND
90	0.13	0.270	0.05	ND
TOK-3	$C_4F_9SO_3$-	$C_4F_9SO_3$-	TDDA	TDDA
1	0.070	0.104	0.51	ND
15	0.070	0.165	0.09***	ND
90	0.13	0.225	ND	0.17

NOTES
*1.8 ppm theoretical maximum
** exceeds theoretical maximum
*** below LOQ
ND = not detected

EXYGEN LIMITS OF QUANTITATION

$C_4F_9SO_3^-$	0.005 ppm
Triethanolamine (TEA)	0.05
Tri-n-dodecylamine (TDDA)	0.100

Table 3. Equilibrium solubility of resist components and byproducts in water, as determined by organic trace analysis. [3]

Compound	Conc (ppm)
PAGs	
TBI-PFBS	31.7
TPS-PFBS	2290
TPS-PFOS	47.6
Dissolution inhibitor	
Lithocholate DI (structure II)	48.8
Photolyisis byproducts	
Iodobenzene	28.7
2-butene	92
tert-butylbenzene	9.7
Extracts from polymer (structure I)	
Acetone	27.1
Isopropyl alcohol	6.9

LeSeur[5] attempted to quantify the amount of PAG extracted from the resist upon contact with water. Using a Clariant (Polymer T2030[4])resist without base quencher and with PAG loading from 0-5% TPS-PFBS, the concentration of PFBS was measured using liquid chromatography mass spectrometric analysis (LCMS). In Figure 5a, the PFBS concentration in the water is plotted as a function of contact time with the resist for each concentration of PAG. The extraction of PAG for the 5% loading stabilizes after 30s for the unexposed and 50s for the exposed samples. The 5ng/cm^2 of PFBS represents approximately 0.3% of the potential 1700ng/cm^2 of available PAG in the contact area of the water droplet.

Figure 5b shows the affect of a deionized water wash prior to the water collection. With a rinse as short as 10s, the extracted PAG in the subsequent samples is approximately 1ng/cm^2, only a quarter of the total PAG extracted without the rinse.

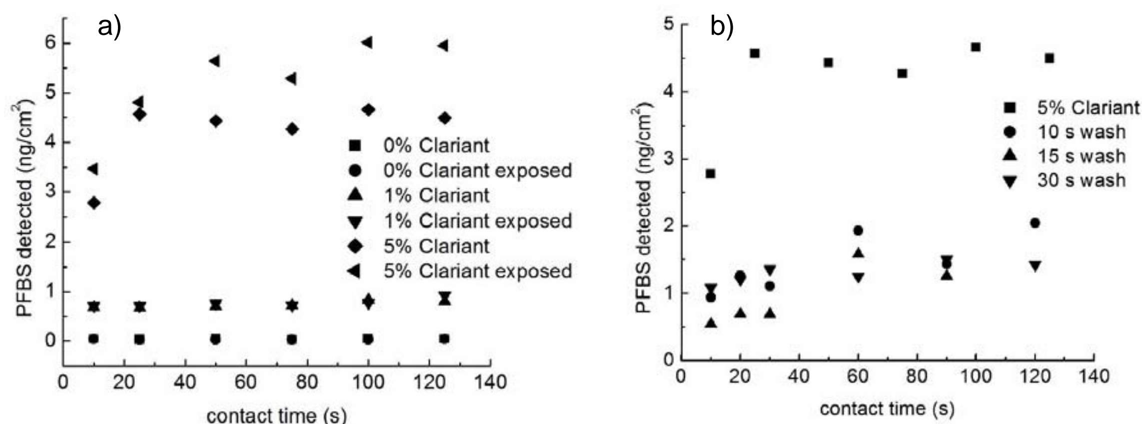

Figure 5. LCMS detection of PFBS leached into the water layer as a function of contact time for a) various levels of PAG loading, for both unexposed and exposed conditions, and b) unexposed resist with 5% PAG loading, for varying pre-exposure washing times.[5]

Kishimura performed resist surface analysis on methacrylate resist with TPS-Nf PAG and triethanolamine base quencher.[1] ToF SIMS (Time of Flight SIMS) analysis was used to compare three resist films, a control sample (not exposed nor immersed), an unexposed immersed sample, and an exposed immersed sample. The ions of SO_2^-, SO_3^-, $C_4F_9SO_3^-$, and $(C_6H_5)_3S^+$ are fragments of TPS-Nf. In Figure 6, the SIMS data demonstrates the leaching of the PAG byproducts, most notably the $(C_6H_5)_3S^+$ ion reduced to ~20% of the control nominal upon immersion and reduced to ~1% with exposure and immersion.

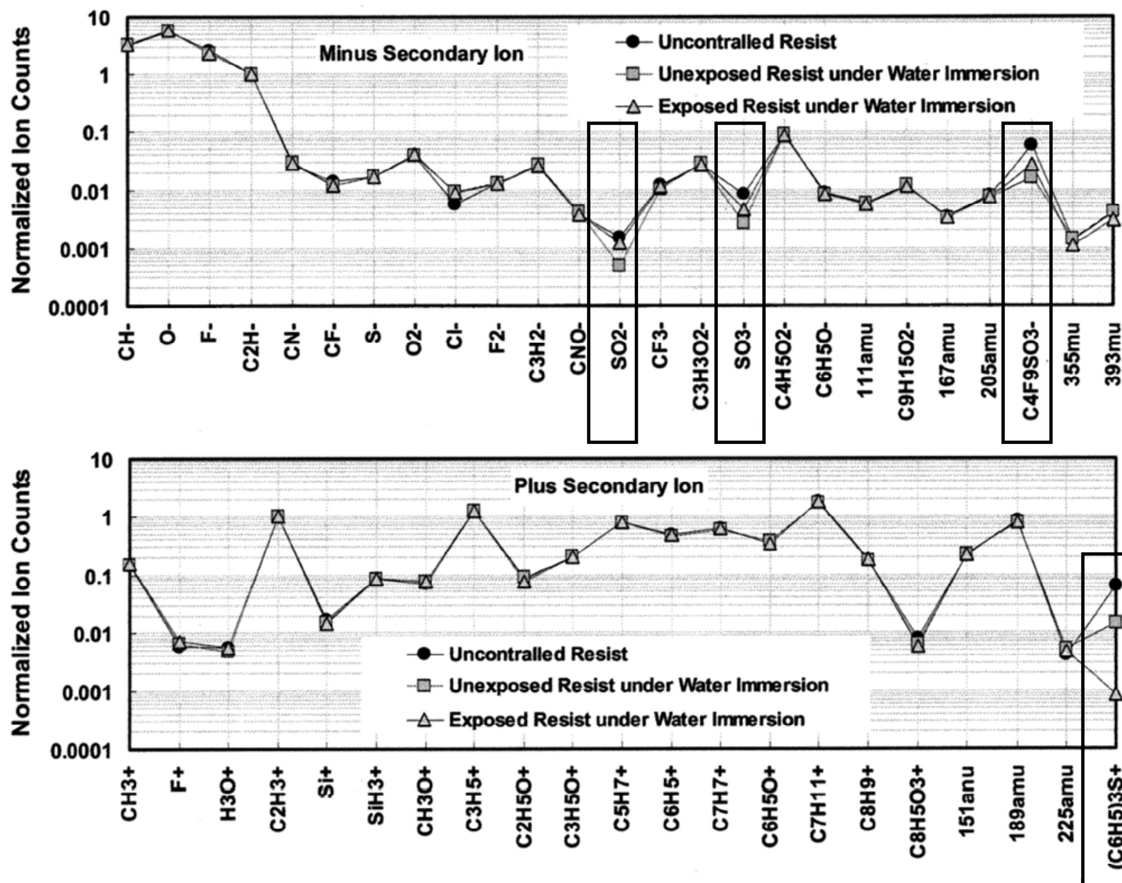

Figure 6. TOF-SIMS data of resist surface analysis of resist immersed in water exposed and unexposed.[1]

4. IMMERSION EFFECTS ON RESIST PERFORMANCE

The primary components of the resist formulation are the polymer resin, the photoacid generator (PAG), and the base quencher. IBM, TOK, and Clariant supplied the resists for these initial studies of the interaction of the resist and water. Each resist has its respective preferences of PAG and base components, perhaps from the optimal experience in dry lithography.

TOK Imaging

The family of TOK resists were supplied to the researchers with two forms of resin (a terpolymer and tetra-polymer), three types of base quencher (small, medium, and large), and a common PAG of TPS-PFBS (triphenylsulfonium perfluorobutanesulfonate or TPS-Nf – triphenyl sulfonium nanoflate).

Table 4. Resist formulations investigated by Raub et al.[4]

		Base Quencher		
		Tri-ethanolamine (Bs)	Tri-pentylamine (Bm)	Tri-octylamine (BL)
Polymer Backbone	Acrylic ter-polymer	TOK-ILP01	TOK-ILP02	TOK-ILP03
	Acrylic tetra-polymer	TOK-ILP04	TOK-ILP05	TOK-ILP06

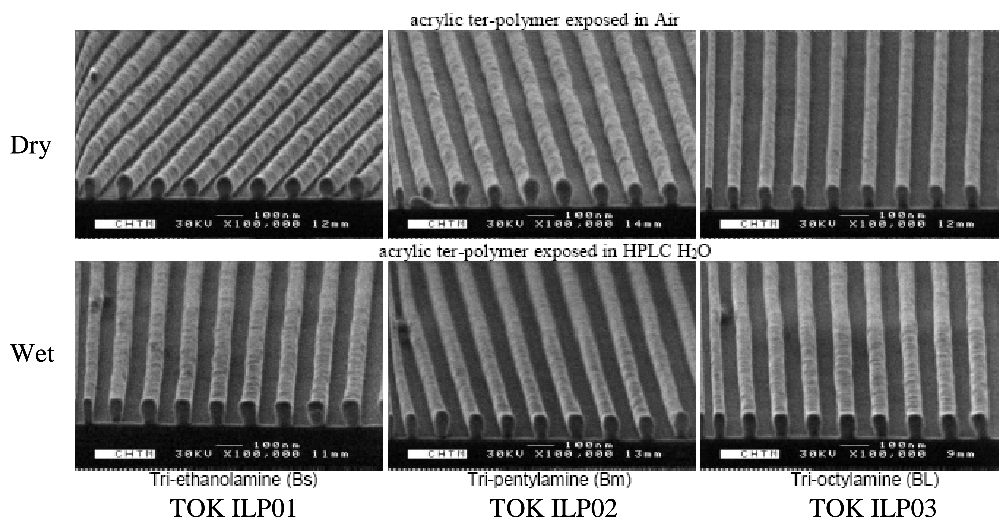

Figure 7. 131nm pitch gratings imaged in TOK ter-polymer for wet and dry lithography.[4]

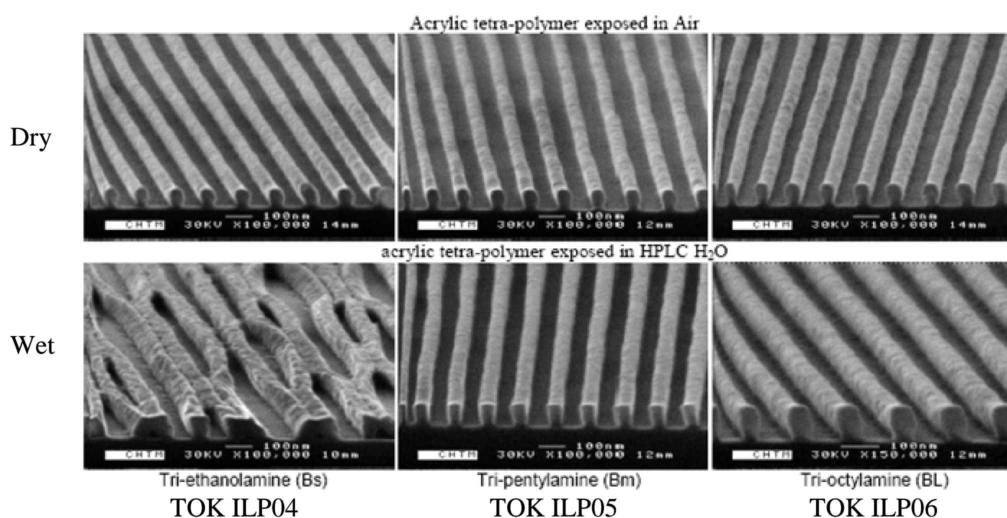

Figure 8. 131nm pitch gratings imaged in TOK tetra-polymer for wet and dry lithography.[4]

In the subsequent analysis, TOK ILP03, the terpolymer with largest base was considered the optimum formulation from this selection of resists. TOK ILP03 is the baseline resist used on the Exitech system at RIT.

Clariant Imaging

The selection of Clariant resists were supplied to the researchers with two forms of polymer resins (a COMA-acrylic hybrid and an acrylic), two base quenchers (small and large), and two PAGs (small and large).

Table 5. Resist formulations investigated by Raub et al.[4]

PAG		TPS-Tf (Ps)		TPS-Nf (PL)	
Base Quencher		Di-ethanolamine (Bs)	Tri-octylamine (BL)	Di-ethanolamine (Bs)	Tri-octylamine (BL)
Polymer Backbone	Hybrid polymer T2030	T2030 Ps Bs	T2030 Ps BL	T2030 PL Bs	T2030 PL BL
	Acrylic polymer T518	T518 Ps Bs	T518 Ps BL	T518 PL Bs	T518 PL BL

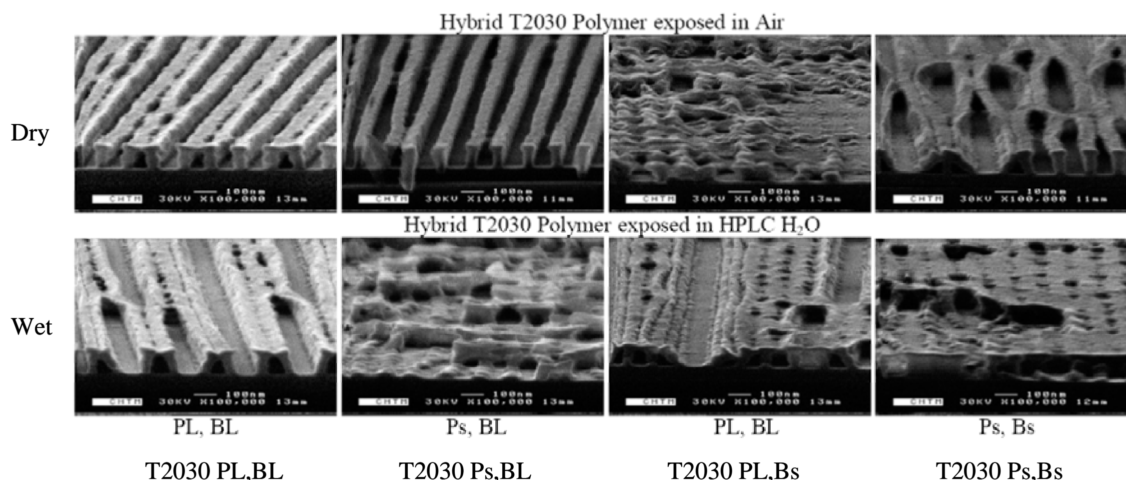

Figure 9. 131nm pitch gratings imaged in Clariant T2030 for wet and dry lithography.[4]

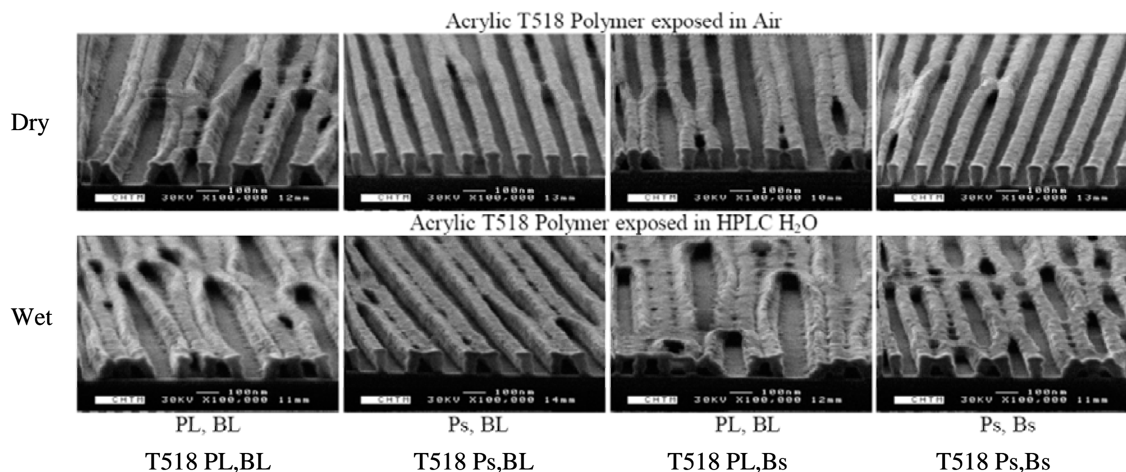

Figure 10. 131nm pitch gratings imaged in Clariant T518 for wet and dry lithography.[4]

In the subsequent analysis, the acrylic T518 outperformed the hybrid T2030. For the T518 resist, the small PAG and large base combination (Ps, BL) performed best.

Kishimura studied the resist interactions with four types of resins; a (meth)acrylate type, a COMA (cycloolefine-mareic anhydride alt-copolymer), a poly(cyclic olefin) type, and a VEMA (vinyl ether-maleic anhydride) type.[1] The mer units for the ArF resins are shown in Figure 1. The dissolution rate of the

formulations of these resists was examined using a resist development analyzer. The results are presented in Figure 11.

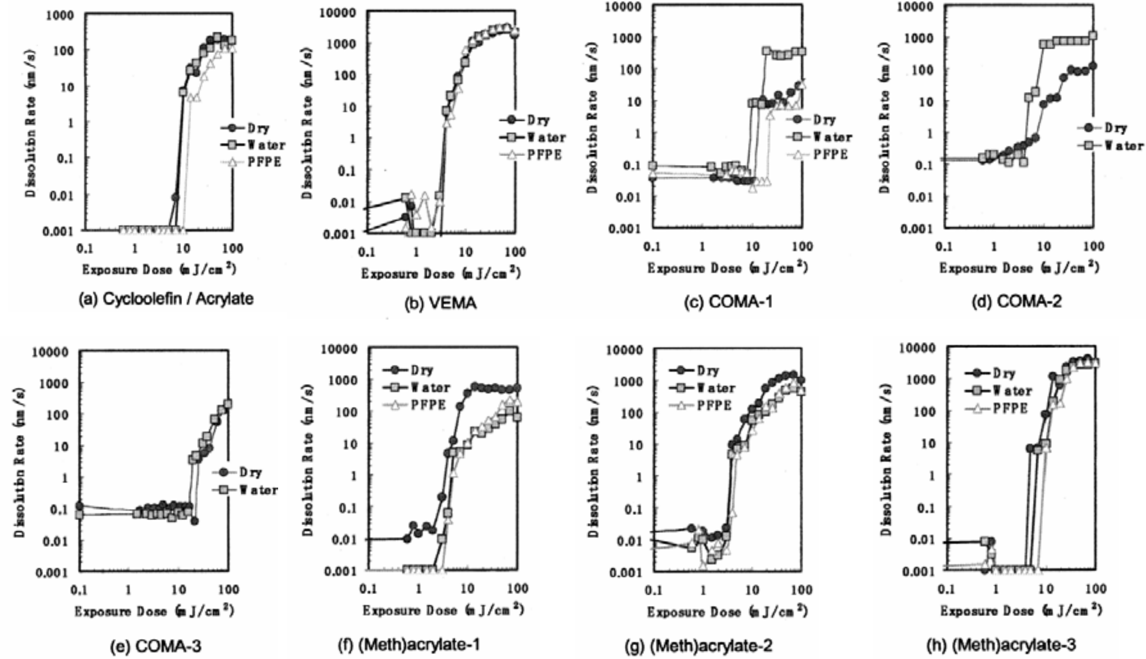

Figure 11. Resist dissolution rate analysis for the resists investigated by Kishimura.

Although the writer does not elaborate on the differences between the formulation of the COMA and (Meth)acrylate series, it is interesting to note the variation in performance that exists with the variations of formulation. A minimal difference between the wet and dry dissolution rates may suggest minimal leaching of the resist components (PAG and base quencher) into the water. For instance, COMA-1 and COMA-2 in Figure 11c and 11d exhibit a much larger variation between the wet and dry dissolution rates in comparison to COMA-3. Similar observations can be made for the (meth)acrylate series in Figure 11f-h, although the overlap between the wet and dry dissolution improves as the series advances. The differences in formulation for the various resists are perhaps the factors to consider in the optimization of materials for immersion lithography.

5. TOPCOAT PROTECTION

The implementation of a topcoat is the ideal solution to suppress and/or prevent the fluid-resist interaction. The design of an ideal topcoat, however, must satisfy many conditions. The topcoat needs to be water insoluble to function in an immersion system, optically transparent at 193nm, TMAH soluble to reduce process complexity, cast in a solvent that has limited reactivity with the resist, and have optical properties to function as a TARC. [6]

TOK TSP3A is fluoro-polymer topcoat that has been used at RIT to protect the resist surface from amine contamination. The practical use of the topcoat is limited by the additional process step needed to remove the topcoat with a proprietary solvent remover. The additional process complexity and cost of material is somewhat prohibitive to industry acceptance.

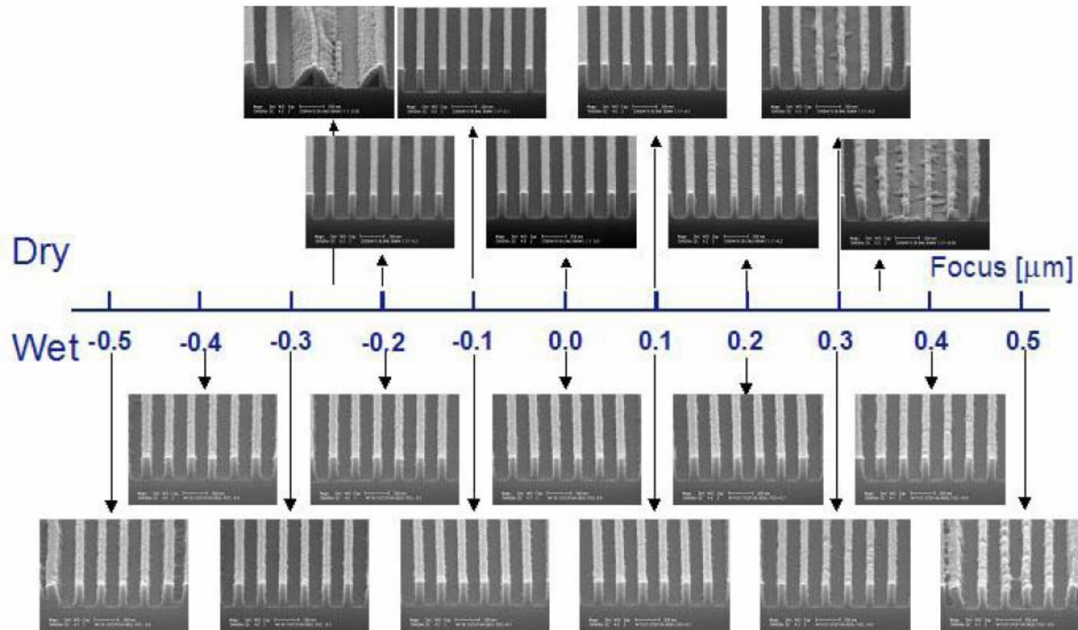

Figure 12. 90nm 1:1 dense lines imaged at ASML using TOK TSP-3A.[7]

5. CONCLUSIONS

Immersion lithography at 193nm is currently the only viable lithographic technology that can keep pace with Moore's law and the technology roadmap from the 65nm node down to the 45nm node. With the incorporation of a water droplet between the final element of the projection lens and the resist stack, the effective NA of an optical system is increased to provide a reduction in the achievable resolution and an extension of the 193nm resist platform.

The water-resist interaction and the subsequent effect on imaging has been the primary concern for the resist chemist. The redistribution and extraction of critical resist components was unknown until recent studies. 65nm 1:1 dense lines have been imaged demonstrating process feasibility without topcoat. From these preliminary studies, polymer resins and effective sizes of PAGs and base quenchers can be sorted to find trends and make adjustments in formulation to improve imaging.

The development of a TMAH developable topcoat is still in the research stage. A hydrophobic fluoropolymer TARC is available but is generally not viewed as an industry solution due to additional process complexity. Until the commercial availability of a developable topcoat is realized, the resist chemist must optimize formulations to compensate for the fluid-resist interaction.

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