

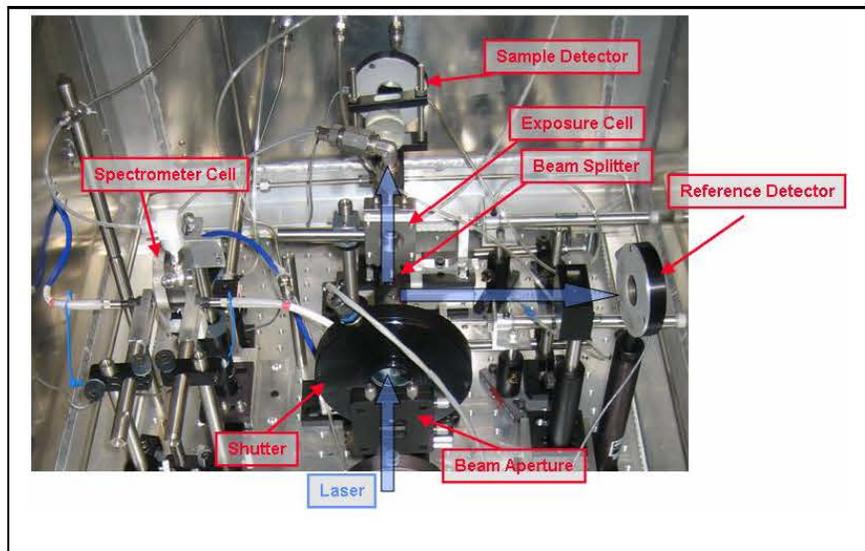
High Index Immersion Lithography With Second Generation Immersion Fluids To Enable Numerical Apertures of 1.55 For Cost Effective 32 nm Half Pitches

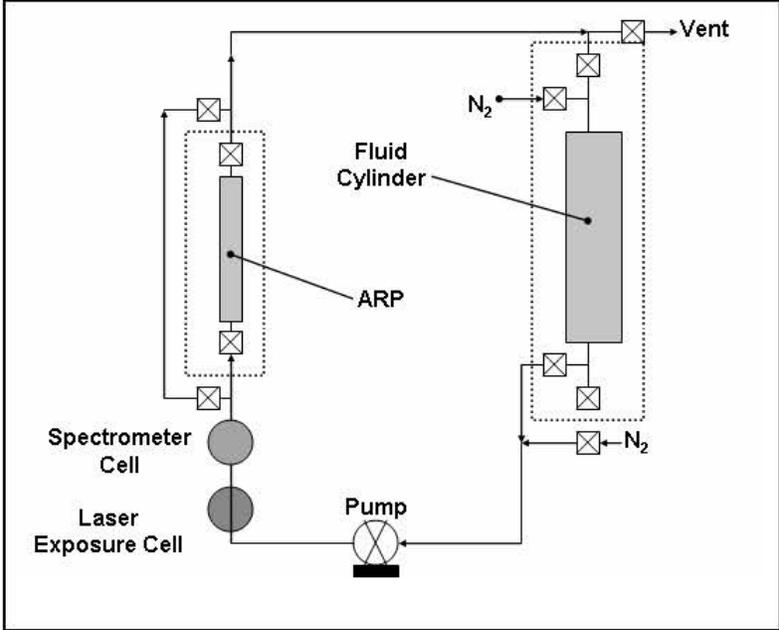
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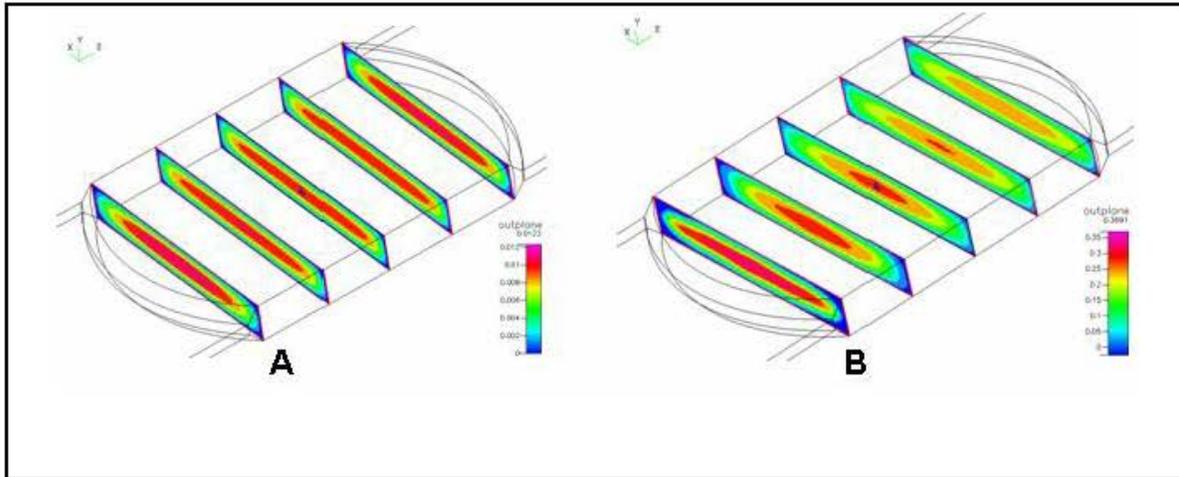
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To identify the most practical and cost-effective technology after water immersion lithography (Gen1) for sub-45 nm half pitches, the semiconductor industry continues to debate the relative merits of water double patterning (feasible, but high cost of ownership), EUV (difficulties with timing and infrastructure issues) and high index immersion lithography (single-exposure optical lithography, needing a suitable high index last lens element [HILLE]). With good progress on the HILLE, high index immersion with numerical apertures of 1.55 or above now seems possible. We continue our work on delivering a commercially-viable high index immersion fluid (Gen2). We have optimized several fluids to meet the required refractive index and absorbance specifications at 193 nm. We are also continuing to examine other property/process requirements relevant to commercial use, such as fluid radiation durability, last lens element contamination and cleaning, resist interactions and profile effects, and particle contamination and prevention. These studies show that both fluid handling issues, as well as active fluid recycling, must be well understood and carefully managed to maintain optimum fluid properties. Low-absorbing third generation immersion fluids, with refractive indices above 1.7 (Gen3), would further expand the resolution of single-exposure 193 nm lithography to below 32 nm half pitch.

Keywords: immersion, second generation fluid, third generation fluid, hydrocarbons, refractive index, absorbance, fluid handling, radiation durability, active recycle, window contamination, particle contamination







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2.3.2 Fluid Dose Metric

To derive a dose metric for a recirculating fluid, we consider a fluid slug as it passes the laser spot in an irradiation cell. For a single pass, the slug dose is expressed in terms of laser repetition rate (R_{las}) and fluid flow rate (F) as

$$\text{Equation 2.} \quad D_{fluid, pass} = R_{las} \times I \times V_{irr} / F$$

In the above, V_{irr} is the total irradiated volume; i.e., for a laser slit width X and height Y , and gap width Z ,

$$\text{Equation 3.} \quad V_{irr} = X \times Y \times Z$$

As the fluid is recirculated, the average dose accumulated by each slug will depend on the total fluid reservoir volume (V)

$$\text{Equation 4.} \quad D_{fluid, tot} = N \times I \times V_{irr} / V$$

Thus, the fluid slug's cumulative dose is the incident dose modified by the volume dilution factor. Note that the units of the fluid dose, just as for the lens element dose, are in energy per area.

2.4 Cross Correlating: The Standard Stepper Tool

The immersion lithography radiation durability methodology and model we have developed for fluid and window lifetimes, is a “presumed” first-order model: initially all

interactions are modeled as linear. Then, as results are obtained based on this model, any non-linear effects will become evident. The Standard Stepper Tool allows the cross correlation of radiation durability results taken using different facilities and experimental parameters. Three facilities, and their general characteristics are summarized in Table 1. The approach is to correlate all the results from different experiments back to a reference “Standard Stepper”, and to thereby compare experimental results according to the number of standard stepper days of fluid or window exposure corresponding to the results.

If different experimental radiation durability results are comparable, then the experiments are within the linear regime for the fluid, or the window, or both. If there are significant differences (using the Standard Stepper correlation) for either the fluid or window metrics, then a non-linear effect is identified.

An example would be experiments run with different values of the laser’s 193 nm energy density (mJ/cm^2). It is well known that energy density is a strongly non-linear term in UV photochemistry processes⁵. If a linear model is used to cross-correlate experiments done at different energy densities, and the modeling results are significantly different from the linear predictions, then non-linear processes are indicated. Then, experiments can be conducted at energy densities typical of lithographic steppers, minimizing this non-linear term. On this basis, we have chosen to use the same energy densities in all experimental facilities, corresponding to that expected at an immersion scanner’s last lens element.

2.4.1 Fluid Metrics: Fluid Flow Rate and Hours For 1 Day Stepper Equivalent

To cross-correlate the dose delivered to the fluid under test (as given by Equation 4), to that delivered to a standard stepper tool, the incident energy load on a fluid as it passes under a scanner slit must be simulated. We accomplish this by matching the fluid flow rate under test to that in a typical scanner tool, as follows:

Table 1. Summary of typical experimental capabilities of three radiation durability test setups at three facilities. The results from these facilities are cross-correlated using the Standard Stepper Tool for both fluid and window output metrics.

Parameter	DuPont	MIT- DP	MIT- Sematech	Std. Stepper
Laser rep rate	200	400	4000	6000
Laser fluence	0.4 - 2.0 mJ/cm^2	0.1 - 0.8 mJ/cm^2	1 mJ/cm^2	0.8 mJ/cm^2
Fluid gap	2-4 mm	2-4 mm	2 mm	3 mm
X _{aperture}	10 mm	4 mm	2 mm	28 mm
Y _{aperture}	5 mm	4 mm	5 mm	7 mm
Y _{cell}	20 mm	20 mm	20 mm	
Flow Rate	cc/min	5 – 80 cc/min	cc/min	1 liter/min
System Vol.	mL	600 mL	mL	
Exp. Time	Hrs	14 Hrs	Hrs	24 Hrs

Equation 5.
$$F_{test} = k \frac{R_{test}}{R_{stepper}} \frac{I_{test}}{I_{stepper}} \frac{V_{irr,test}}{V_{irr,stepper}} F_{stepper}$$

In Equation 5, k refers to the NA scaling factor (the difference between effective NA in a scanner and a test setup) and can be taken close to 1; the other parameters are as defined in section 2.3 above.

For example, assume a stepper flow rate of 1 liter per minute (lpm), a laser repetition rate of 6000 Hz, a laser slit of 7 by 28 mm and a fluid gap of 3 mm. Then, as described in section 2.1, and matching the incident fluence to the stepper's, we obtain from Equation (5) that $F_{test} = 0.005$ lpm.

Once the flow is matched appropriately, we can determine an equivalent dose for a test setup to obtain 24 hours of stepper use, by matching total doses of the two setups using equation (4). If we write the total number of pulses in terms of laser repetition rate and time exposed, t , as follows:

Equation 6.
$$N = R \times t$$

then, from (4) and (6), we can derive:

Equation 7.
$$t_{test} = \frac{R_{stepper}}{R_{test}} \frac{I_{stepper}}{I_{test}} \frac{V_{irr,stepper}}{V_{irr,test}} \frac{V_{test}}{V_{stepper}} t_{stepper}$$

For example, given a test reservoir of 1/2 liter and a stepper reservoir of 100 liters, and other parameters as above, we find that 24 hours of stepper time can be represented by 22 hours of test time

2.5 Output Metrics: Window And Fluid Lifetimes

2.5.1 Fluid Degradation

To determine fluid degradation, we monitor fluid transmission through the downstream spectrometer as a function of fluid dose, according to Equation (4). Analyzing induced fluid absorbance per cm (base 10), we observe two behavior types: initial absorbance decrease, followed by later absorbance increase (see Figure 4). Assuming that both fluid darkening (with a pre-exponential of a_d and an exponential rate of r_d) and bleaching (with a_b and r_b) are operative, we fit the induced fluid absorbance (A_{ind}^I) to a dual exponential, where the starting induced absorbance is zero, by definition:

Equation 8.
$$A_{ind}^I = a_d e^{r_d D} + a_b e^{-r_b D} - a_d - a_b$$

Now, we define fluid end-of-life for this example as a 5% transmission degradation over a 3 mm gap. Using the exponential fit of equation 8, we can then calculate the fluid lifetime dose for each set of experimental conditions.

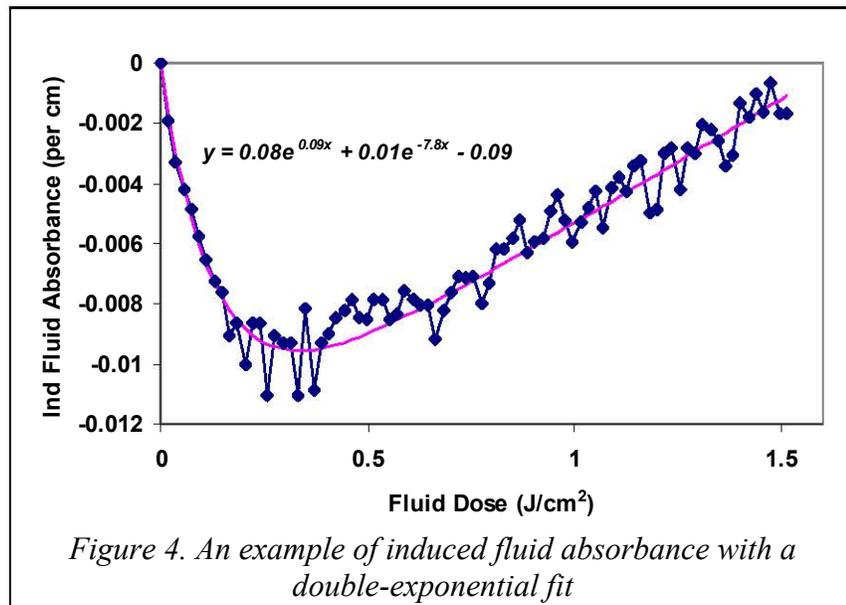
2.5.2 Window Contamination

Once a fluid's induced absorbance is known from downstream cell measurements, we can separate the window contribution from the total cell transmission drop measured by 193-nm laser. Unfortunately, for our experimental conditions, the window degradation rate was too small to reliably be decoupled with our in-situ diagnostics. Instead, window

transmission was measured offline (spectrophotometry) after the irradiation. In these measurements, we compared an irradiated area to an unirradiated area of a front cell window, and calculated an induced absorbance rate, based on the window's total dose, as calculated from equation (1). Once the rate is known, we calculate window dose to achieve a 5% transmission drop for a single window: the window lifetime dose

3 Radiation Durability of A Gen2 Immersion Fluid

Using the present radiation durability methodology, and the Standard Stepper Tool approach, we have performed a screening design of experiment (DOE) study. The study's goal was to determine, from the fluid and the window responses, the important factors in a representative Gen2 immersion fluid's radiation durability.



3.1 Design Of Experiment

The DOE study was conducted in the MIT-DuPont radiation durability facility, whose characteristics are summarized in Table 1. The tests were all run for 13.9 hours of laser exposure time; the fluid absorbance, in-situ cell transmission by laser radiometry, and the front and back window transmissions were measured. Each run's experimental results were analyzed using the Standard Stepper Tool.

3.1.1 Factors or Input Metrics

The screening DOE was organized to study five input parameters at two levels: Energy Density (0.8 mJ/cm² or 0.1 mJ/cm²), the Fluid Absorbance (0.06/cm or 0.11/cm), Active Recycle (present or absent), Fluid Layer Thickness (2 mm or 4 mm), and the Fluid Flow Rate (high or low).

3.1.2 Responses or Output Metrics

The experimental doses delivered to the fluid cell were insufficient to produce measurable induced absorbance in the cell windows, so window effects are not reported from this DOE. Instead, the five input parameters were evaluated for the fluid. As response metrics, the Fluid Dose for ΔT=5%, and the pre-exponential factors and rate exponents for the fluid's darkening and the bleaching processes, were chosen..

We also report the fluid lifetime in the standard stepper, from the cross correlations of the MIT-DuPont facility to the Standard Stepper Tool.

3.1.3 Results

For illustrative purposes, the results from two DOE runs are summarized Table 2. These runs have differences in fluid absorbance, the presence of active recycle, and the

fluid flow rate. The experiments' fluid dose was fixed at 1.5 J/cm². The output metrics for these two runs vary by an order of magnitude.

3.1.4 Principle Effects

From the initial DOE runs, the Fluid Flow Rate and Fluid Thickness showed only minor effects, and were removed from the DOE analysis (even though they were variables in all of the runs).

From the fluid dose for 5% ΔT, the effects (in order of decreasing importance) were Active Recycle, Energy Density, and Fluid Absorbance. From the darkening rate exponent analysis, the Energy Density was a principle effect. Finally, from the bleaching pre-exponential factor, the Fluid Absorbance was the most important effect.

Table 2. Illustrative Results from DOE Runs 1 and 2		
Input Parameters	Run 1	Run 2
Energy Density (mJ/cm ²)	0.8	0.8
Fluid Absorbance (1/cm)	0.06	0.11
Active Recycle	Present	Absent
Fluid Thickness (mm)	4	4
Fluid Flow Rate	Low	High
Fluid Dose		
Total Fluid Dose (J/cm ²)	1.5	1.5
Output Metrics		
Fluid Dose For 5% ΔT	7.9	0.59
Fluid 5% ΔT Stepper Lifetime (Days)	> 4 days	< 0.5 days

4 Resist Interactions and Immersion Defectivity

Several defectivity issues must be addressed to enable the practical use of high index fluids for immersion lithography. In water immersion lithography, a topcoat is likely needed due to photoacid generator (PAG) leaching, which could have detrimental effects on resist thickness changes, profile changes, and/or final lens element contamination. The same issue needs to be considered when moving to higher index fluids: how much leaching of PAG occurs from the resist into Gen2 immersion fluids.

4.1 Leaching and Film Effects

With water as the immersion liquid, reports in the literature⁶⁻⁹ have shown that as much as 100 ppb of either exposed or unexposed PAG can leach into water in 60 seconds. Two stepper companies have set limits on the amount of PAG that can be tolerated (ASML = 1.6 x 10⁻¹² mol/cm²-sec, Nikon = 5.0 x 10⁻¹² mol/cm²-sec), due to potential lens

contamination. We have studied the amount of PAG leaching into three of our second generation immersion fluid candidates.

As shown in Figure 5 and Table 3, the PAG leaching level from a commercial resist into three of our Gen2 fluids was much less than that for water, when the resist film (thickness of 150 nm, 2 cm² contact area) was exposed to the fluid (3 mL) for up to 60 seconds. The PAG was detected via liquid chromatography / mass spectrometry / mass spectrometry (LC/MS/MS)⁶ in negative ion mode. In another study, we have seen comparable PAG

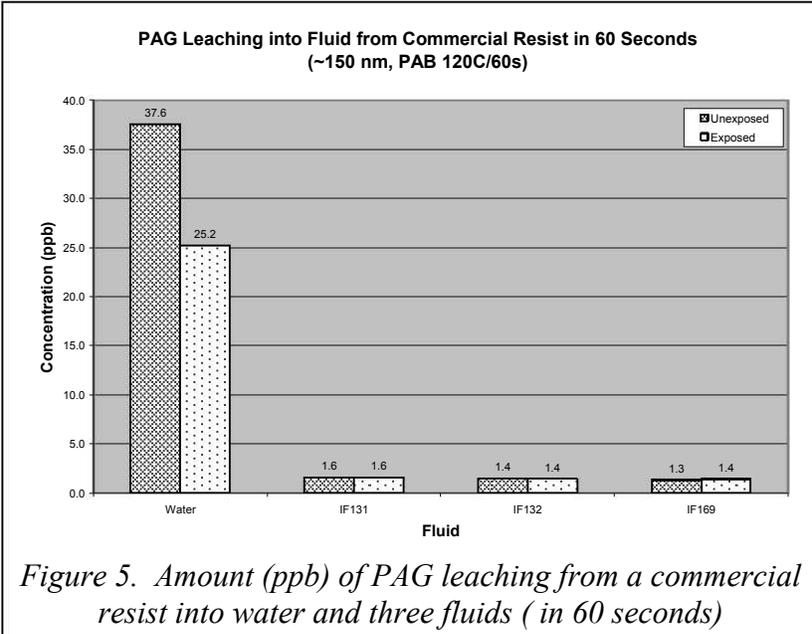


Figure 5. Amount (ppb) of PAG leaching from a commercial resist into water and three fluids (in 60 seconds)

leaching levels into Gen2 fluids and water when a longer contact time is used with a larger contact area. Further experiments are underway to determine the leaching of other resist components, such as base and dissolution modifiers, into the Gen2 immersion fluids

The solubility limit of this particular PAG in both water and the three high index

Fluid	Ppm
Water	4.58
IF132	3.37
IF131	1.80
IF169	1.79

immersion

fluids was also investigated (Table 4). The PAG's solubility limit in water is higher than in the Gen2 fluids. However, even in the latter liquids, the PAG concentration is in the ppm range – although very little is seen to leach into the fluid from the resist film at short contact times.

Fluid	Concentration (mol/cm ²) in 60 seconds	
	Unexposed	Exposed
Water	7.72E-11	5.18E-11
IF131	3.22E-12	3.22E-12
IF132	2.96E-12	2.93E-12
IF169	2.69E-12	2.89E-12

5 Progress Towards Gen3 Immersion Fluids

5.1 Correlations Of d-line and 193 nm Index Of Refraction

Refractive index data has been collected for several dozen materials at wavelengths between 589 and 193 nm. The materials range from solutions of inorganic salts in water, to organometallic compounds, to organic compounds (both neat and in IF132). Some compositions were found with absorption onsets of less than 210 nm; of these, several

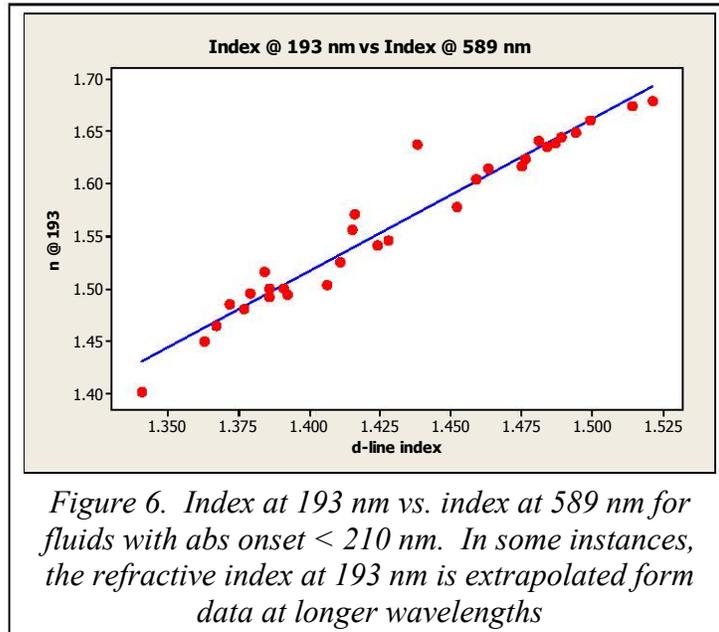
had absorbances of $< 20 \text{ cm}^{-1}$ at 193 nm. Interestingly, despite the diversity of chemical compositions, a plot of index at 193 nm vs. 589 nm (d-line index) affords a reasonably straight line (*Figure 6*).

Using the *Figure 6* data, we can derive an empirical relationship between index at 193 nm and d-line index:

Equation 9
$$n(193 \text{ nm}) = 1.48 n(589.3 \text{ nm}) - 0.56$$

This relationship is useful, since d-line refractive indices are known for many materials. Using this equation, one can estimate the d-line index value corresponding to a given 193 nm index.

As shown in Table 5, a Gen3 fluid ($n > 1.70$) will likely have a d-line index of > 1.56 . There are liquids known to have high refractive indices at 589 nm (e.g., for bromoform $n_D^{20} = 1.595$); however, none (to our knowledge) are also acceptably transparent at 193 nm.



5.2 Approaches to Gen3 Immersion Fluid

One approach to a Gen3 fluid involves dissolving high index materials in water. We have surveyed saturated aqueous solutions of main group and lanthanide metal salts, and have found that most had refractive indices of less than 1.6 @ 193 nm. In general, refractive index and absorbance appeared to be a function primarily of the anion, and less dependent on the nature of the cation. Polarizable anions such as halides gave higher refractive indices but also higher absorbances at short wavelengths; less polarizable anions (e.g. sulfates, methanesulfonates, tetrafluoroborates) gave lower refractive indices but higher transparency. Thus, a 50 wt% (29 vol%) solution of anhydrous ZnCl_2 in water has an absorption of $> 500 \text{ cm}^{-1}$ and an (extrapolated) index of 1.64 at 193 nm (its absorption onset is 200 nm). On the other hand, 33 wt% (17 vol%) $\text{Zn}(\text{O}_3\text{SMe})_2(\text{H}_2\text{O})_{4.4}$ in water has an absorption of 5.3 cm^{-1} , but an index of

589 nm (d-line) Index	Predicted 193 nm Index
1.46	1.60
1.49	1.65
1.53	1.70
1.56	1.75
1.59	1.80

only 1.48 at 193 nm. Similarly, a 50 wt% solution of $Zn(O_3SCF_3)_2$ in water has a relatively low absorption of 5.4 cm^{-1} at 193 nm, but an index of only 1.465

A more promising route to high index, highly transparent fluids involves identifying new hydrocarbocyclic or “organometallic” materials that are either relatively non-viscous fluids, or which dissolve in and raise the refractive index of current Gen2 fluids. For example, we have synthesized pure hydrocarbon and organosilicon fluids with 193 nm refractive indices as high as 1.68 ($n_D^{20} \approx 1.52$) and $Abs < 50 \text{ cm}^{-1}$ at 193 nm. While still short of Gen3 fluid requirements, these results suggest that fluids with incrementally higher refractive indices than current Gen2 candidates are possible.

5.3 Structure Design Factor For The 193nm Refractive Index

In designing immersion fluids, we use a physical parameter which we will call the Structure Design Factor. A plot of d-line index for materials that are transparent at 193

nm versus this physical parameter is linear. As shown in Figure 7, both solids, and also Gen2 and organosilicon fluids, fall on this line. Note that an organosilicon fluid with a somewhat higher d-line index than a Gen2 fluid has been identified ($n_D^{20} 1.52$ vs.

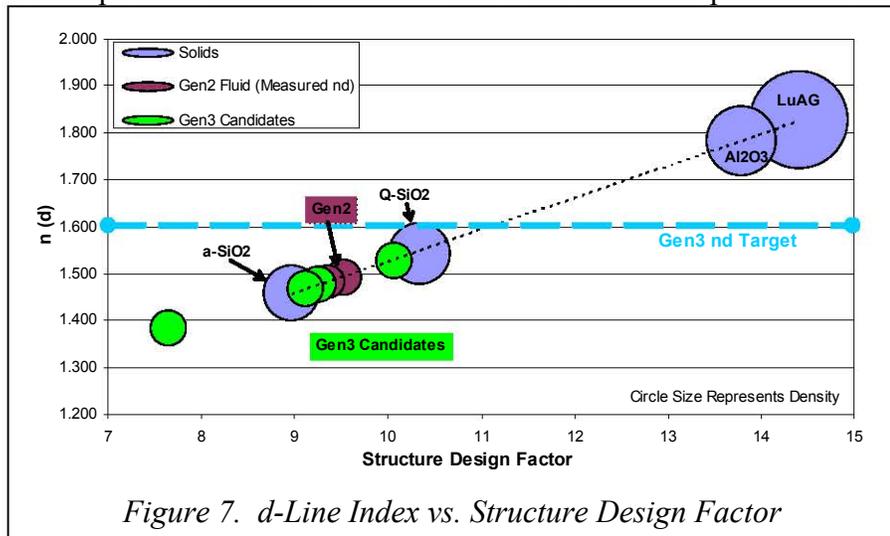


Figure 7. d-Line Index vs. Structure Design Factor

~1.48 for Gen2); nevertheless, its d-line index does not meet the particularly-desirable target d-line index of ~1.59 (which would correspond to a 193 nm index of ~1.8; see Section 5.1).

6 Conclusions

Substantial progress has been made in understanding the factors responsible for Gen2 immersion fluid photodegradation, and systems to correct such degradation have been developed and successfully tested. The development of appropriate metrics has been found to be critical to assessing the results of such studies. As for the Gen1 fluid, water, interactions studies of fluids in contact with process surfaces such as photoresist are essential to these Gen2 fluids’ manufacturing insertion. Desirably, we find much less PAG leaching into these fluids compared to water. Finally, our studies of post-Gen2 fluids have identified factors which correlate to index, and have allowed us at this point to define fluids whose 193 nm indices approach 1.7 – an improvement over the current candidates in most intense development, but still short of the industry’s current Gen3 goal.

7 Acknowledgements

The authors would like to acknowledge G. Nellis and S. Schuetter of University of Wisconsin, Mechanical Engineering Department for the computational fluid dynamics, and Louis Markoya Of ASML-Wilton for the fluid flow cell.

The MIT-LL portion of this work was sponsored by a Cooperative Research and Development Agreement between MIT Lincoln Laboratory and DuPont Corporation. Opinions, interpretations, conclusions and recommendations are those of the authors and not necessarily endorsed by the United States Government.

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