Index of refraction of high-index lithographic immersion fluids and its variability

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Abstract. We have developed a number of second-generation high-index candidate immersion fluids that exceed the 1.6 refractive index requirement for immersion lithography at 193 nm to replace the water used in first-generation immersion systems. To understand the behavior and performance of different fluid classes, we use spectral index measurements, based on the prism minimum deviation method, to characterize the index dispersion. In addition to fluid absorbance and index requirements, the temperature coefficient of the refractive index is a key parameter. We have used a laser-based Hilger–Chance refractometer system to determine the thermo-optic coefficient (dn/dT) by measuring the index change versus temperature at two different laser wavelengths, 632.8 and 193.4 nm. Also, we determined the batch-to-batch (within a 6-month period), before and after irradiation (at 193.4 nm), before and after air exposure, and before and after resist exposure (image printing test) variations of index and Δn/ΔT. The optical properties of these second-generation immersion fluids mostly compare favorably to water; the ratio of index of refraction at 193.4 nm is 1.644/1.437, the dispersion from d-line (Δn_93.4) is 0.160 versus 0.103 and dn/dT at 193.4 is −550 × 10⁻⁶/K vs. −93 × 10⁻⁶/K, respectively. © 2009 Society of Photo-Optical Instrumentation Engineers. [DOI: 10.1117/1.3124189]

Subject terms: lithography; index; temperature coefficient of the refractive index
Paper 08058R received Jun. 27, 2008; revised manuscript received Nov. 14, 2008; accepted for publication Mar. 16, 2009; published online May 1, 2009.

1 Introduction

The optical properties of high-index immersion fluids, including optical absorbance, refractive index, thermo-optic coefficient, and variation of index, are critical to their use in immersion lithography. Transparency is a key requirement for immersion fluids for four major reasons: (i) to maximize the incident light on the photoresist, (ii) to minimize photoinduced fluid degradation, (iii) to minimize the photo-induced fluid temperature increase, and (iv) to prevent transmission apodization, a variation of transmission with different illumination angles. Saturated hydrocarbon alkanes can have high transparency, and cyclic alkanes with different carbon numbers have higher indices than linear alkanes of the same carbon number.

Here, we report measured values of the refractive index, thermo-optic coefficient, and variation of the index of second-generation immersion fluids with oxygen exposure, irradiation, resist exposure, and isomeric change, as well as Δn/Δλ values for the second-generation immersion-fluid candidates. The spectral index measurements were performed with the prism minimum-deviation method, while the measurements of thermo-optic coefficient (dn/dT) and variation of index were performed with a laser-based Hilger–Chance refractometer system.

2 Experimental

2.1 Spectral Index of Refraction Measurement

The minimum-deviation technique is commonly used to measure refractive indices of optical materials with low uncertainty. In our setup, a hollow stainless steel prism with ports to allow fluids to be exchanged is used to contain the liquid under test. The fluid cavity is defined by two transparent windows made through clear windows of CaF₂. If the windows have parallel surfaces, the effects of the

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opposite window surfaces on the refraction of each window are completely cancelled out in the symmetric cell, so the measured deviation angle is due only to the fluid in the cell. Light passing through the prism is refracted, and the angle of refraction can be used as a measure of the fluid refractive index, as shown in Fig. 1.

Performing the minimum-deviation experiment requires continuous variable-angle capability with high resolution. Because highly accurate goniometer systems are employed on research spectroscopic ellipsometers, it is possible to adapt the prism minimum-deviation technique to variable-angle ellipsometer systems. Measurements are possible at any wavelength where the fluid and the cell windows are semitransparent. It is possible to set the wavelength at discrete values or perform continuous wavelength scans over a wide spectral range. In the enclosed prism cell fluid, flow is not a problem, and the cell is capped to avoid evaporation or contamination.

Measurements reported here were performed using a J. A. Woollam DUV-VASE spectroscopic ellipsometer system at Dupont capable of continuous-angle operation from 10 to 90 deg and over the spectral range of 170–1000 nm. The light source can be set to discrete wavelengths or continuously varied over this spectral range in order to target particular wavelengths of interest or determine a continuous index dispersion curve. The room temperature was between 20 and 23 °C for all measurements, monitored using a temperature sensor. The measurements were corrected to 21.5 °C using the thermo-optic coefficients of water, from Burnett and Kaplan \[dn/dT(193 \text{ nm}) = -0.0001 \text{ °C}^{-1}\], and the thermo-optic coefficients for the high-index fluids, determined in this work. If the temperature during measurements of water was 23 °C, for example, the refractive index can be corrected to room temperature 21.5 °C by adding 0.00015 to the original index measurement to account for the 1.5 °C offset.

For these measurements, the liquid-filled prism cell was mounted on the sample stage, as shown in Fig. 2. The ellipsometer then determined the minimum-deviation angle for light transmitted through the prism at each wavelength. The spectral range is from 2.01 eV (616.8 nm) to 6.41 eV (193.4 nm) in steps of 0.4 eV. A light beam of wavelength \(\lambda\) passes through a prism with a known apex angle \(\alpha\). By orienting the prism so that the light travels symmetrically through the prism, the deviation angle \(\delta\) is at a minimum. If \(n_{\text{gas}}\) is the index of the surrounding ambient, then the fluid refractive index, \(n_{\text{fluid}}(\lambda)\), is given by:

\[
n_{\text{fluid}}(\lambda) = \frac{\left(\frac{\alpha + \delta(\lambda)}{2}\right)}{\sin\left(\frac{\alpha}{2}\right)} n_{\text{gas}}(\lambda)
\]

The minimum-deviation prism index measurement uncertainty is typically \(\pm 300 \times 10^{-6}\), even though the method can in principle be accurate to \((1 \pm 10) \times 10^{-6}\).

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When designing high-index immersion fluids, it is useful to consider the different contributing factors to the index of refraction at the lithographic wavelength. It is also useful to consider the d-line index and the spectral dispersion of the index independently, because these two terms can vary relatively independently with fluid physical properties.

### 2.2 Thermo-optic Coefficient and Index-Variation Measurements

Measurements of the thermo-optic coefficient and sample-to-sample index variation were performed using a laser-based Hilger–Chance refractometer at the National Institute of Standards and Technology (NIST), shown in Fig. 3, which has been described previously. The heart of the device is a 90 deg. inverted-prism cell with a volume of 0.4 cm\(^3\) made from modified fused silica glass, which is temperature-controlled to within \(\pm 0.02 \text{ °C}\). The refractive index of the fluid is derived from the measured angular beam deviation through the filled cell, using known values of the refractive indices of air and the glass prism material, and the precise angles of the prism faces. In these measurements, the source of radiation was either a 632.8 nm HeNe gas laser or a 193.4 nm ArF excimer laser.

The thermo-optic coefficient, \(dn/dT\), was measured by filling the cell, allowing it to thermally stabilize at 21.5 °C for approximately 20 min, varying the sample temperature by 0.5 to 1.0 °C, and recording the change in angular deviation through the cell. Sample-to-sample variation in \(n\) was measured at 20 °C by alternately filling the cell with a...
“reference” fluid and several other fluids under study, again allowing 10–20 min for thermal equilibrium, and recording the change in angular deviation through the cell. The uncertainty in the measured value of \( n \) is dominated by the alignment of the inverted prism cell to the input beam. The expanded uncertainties (\( k=2 \)) in \( n \) are estimated to be \((300–600) \times 10^{-6}\). The uncertainties in \( \Delta n/dT \) are in the range of \((10–70) \times 10^{-6}/K\), while the uncertainties in recorded sample-to-sample variation are approximately \((12 to 50) \times 10^{-6}\). The dominant sources of uncertainty are drifts in mechanical alignment and temperature.

3 Results and Discussion

3.1 Spectral Index of Refraction

Four different candidate high-index immersion fluids were studied, designated by their development names as IF131, IF132, IF138, and IF169. They consist of cyclic alkane molecules with different compositions. The spectral index of refraction for each fluid and water is shown in Fig. 4. Each fluid has been measured at the wavelengths at which it is transparent.

Table 1 shows the index of refraction of water at 193.4 nm (\( n_{193} \)) with the d-line index (\( n_d \)) and the dispersion (\( \Delta n_{193,d} \)), where \( \Delta n \) is defined as \( \Delta n_{193,d}=n_{193}-n_d \).

Table 1 Index of refraction measured at Dupont.

<table>
<thead>
<tr>
<th>Fluid</th>
<th>( n ) at 193.4 nm</th>
<th>( n ) at 589.3 nm</th>
<th>( \Delta n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.437</td>
<td>1.333</td>
<td>0.104</td>
</tr>
<tr>
<td>IF131</td>
<td>1.641</td>
<td>1.476</td>
<td>0.165</td>
</tr>
<tr>
<td>IF132</td>
<td>1.644</td>
<td>1.481</td>
<td>0.163</td>
</tr>
<tr>
<td>IF138</td>
<td>1.615</td>
<td>1.463</td>
<td>0.152</td>
</tr>
<tr>
<td>IF169</td>
<td>1.656</td>
<td>1.491</td>
<td>0.165</td>
</tr>
</tbody>
</table>

Accuracy \( \approx 2 \times 10^{-3} \), no explicit temperature control

From this, we see that the 193.4 nm index of water (1.437) consists of a d-line index of 1.333 and a \( \Delta n_{193,d} \) of 0.104. These two contributions to the lithographic index are useful material parameters when comparing different fluids.8,16

Table 2 shows the values of refractive index with \( \approx 10 \times 10^{-6} \) uncertainty for four of our immersion fluids, with water listed as well for reference. A trend in the data can be noted in that all the immersion fluids have higher indices of refraction than water. IF169 has a d-line index of 1.491, and water has an index of 1.333. The dispersion \( \Delta n_{193,d} \) of IF169 is 0.165, which is much larger than the dispersion of 0.104 for water, and from this, the index of refraction of IF169 is 1.656 at 193.4 nm, a substantial improvement on water’s index of 1.437. Compared to other tested fluids, IF132 has the second highest index at 193.4 nm, 1.457, with a dispersion \( \Delta n_{193,d} \) of 0.163 and the lowest base 10 absorbance3 of 0.03/cm. IF132 is useful in the context of high-index immersion lithography due to these properties along with its high 193 nm radiation durability.6

3.2 The Thermo-Optic Coefficient, \( dn/dT \)

In addition to fluid absorbance and index requirements, the temperature coefficient of the refractive index is a key parameter. We used the laser-based Hilger–Chance refractometer to determine the thermo-optic coefficient (\( dn/dT \)) by measuring the index change versus temperature at two different laser wavelengths, 632.8 and 193.4 nm, as shown in Table 2. A statistical uncertainty analysis was used to determine the \( dn/dT \) measurement variance. The refractive index and the thermo-optic coefficient of distilled water were also measured to check the instrument calibration and repeatability; the results agreed with published data5 to within the uncertainties of the present measurements.

The values of thermo-optic coefficients of these immersion fluids, on the order of \(-550 \times 10^{-6}/K\), are \( \approx 5 \) times larger in magnitude than that of water, which may have implications for their use in high-resolution stepper systems where the temperature would have to be controlled with millikelvin stability.

3.3 Variational Studies of the Index of Refraction

Stability of the optical properties such as the index of refraction of immersion fluids is another important factor for...
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Table 3 Batch-to-batch index-variation.

<table>
<thead>
<tr>
<th>Sample ID (reference sample in bold)</th>
<th>(\Delta n) from reference sample ((10^{-6})) 20°C at 193.4 nm</th>
<th>Uncertainty in (\Delta n) ((2\sigma) (10^{-6}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF132-A</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>IF132-B</td>
<td>-5</td>
<td>12</td>
</tr>
<tr>
<td>IF132-C</td>
<td>4</td>
<td>12</td>
</tr>
<tr>
<td>IF132-D</td>
<td>-14</td>
<td>19</td>
</tr>
<tr>
<td>IF132-E</td>
<td>-11</td>
<td>25</td>
</tr>
<tr>
<td>IF132-F</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>IF169-A</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>IF169-B</td>
<td>-15</td>
<td>24</td>
</tr>
<tr>
<td>IF169-C</td>
<td>-3</td>
<td>20</td>
</tr>
</tbody>
</table>

 advanced lithographic applications. A total of 24 samples of immersion fluid were studied to determine the variation of index in specimens that were collected over a period of 6 months. Table 3 shows results of the index and \(\Delta n\) at 20 °C and 193.4 nm, with the best estimates for the uncertainties, based on analyzing the stability of the measurement system for IF132 and IF169.

For each batch of fluids that we studied, we defined a “reference” sample (indicated in bold in Table 3) that we measured three times in the IF132 case or twice in the IF169 case. We recast the data as \(\Delta n\), the difference of each sample’s index from the average value that we measured for the reference sample for that series. The units of this index variability or uncertainty are \(10^{-6}\).

IF132 has an uncertainty of \(25 \times 10^{-6}\) in batch-to-batch index variation. For the IF132 series, all the samples are the same within the \(2\sigma\) error bars. However, there does seem to be a reproducible and reversible decrease in index on exposure to air for several hours, slightly larger than the uncertainty in the repeated measurements.

IF169 has an uncertainty of \(24 \times 10^{-6}\) in batch-to-batch index variation. For the IF169 series, we saw no significant differences among samples.

Table 4 shows the difference in index for samples of IF132 before and after radiation. The radiation-exposed sample has an uncertainty of \(16 \times 10^{-6}\) in variation of index.

The variations of index for a sample before and after air exposure are shown in Table 5. For all of the air-exposed samples, there was also a quite-noticeable decrease (\(\Delta n = -45 \times 10^{-6}\)) that went away as well when the fluid was stored in nitrogen box overnight (\(\Delta n = 2 \times 10^{-6}\)). The average change in index on exposure to air appears to be about \((-28 \pm 22) \times 10^{-6}\) (\(2\sigma\)). The optical absorbance IF132 increases from 0.03/cm in the absence of air (in a dry nitrogen environment) to 0.9/cm when exposed to air, and this change in the optical absorbance can lead to a Kramers–Kronig coupled change in the index of refraction.\(^{16}\)

Table 6 shows the before and after resist exposure variations in index. For the resist-exposed sample, the index variation is slightly larger (\(\Delta n = -12 \times 10^{-6}\)) compared to the before-resist-exposed sample (\(\Delta n = 2 \times 10^{-6}\)).

Some cyclic alkanes can have multiple isomers, for example, the cis and trans isomers of decalin, and differences in the index of refraction of the different isomers can be a large source of variability in the index of refraction. Decalin can be either isomerically pure or a mixture of isomers, such as 77% cis and 23% trans-isomers. The trans-isomer is more stable because of less steric interactions. However, the trans-isomer of decalin has a lower value of index refraction.

Table 4 Index variation due to excimer laser irradiation.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>(\Delta n) from reference sample ((10^{-6})) 20°C at 193.4 nm</th>
<th>Uncertainty in (\Delta n) ((2\sigma) (10^{-6}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF132-A(^{a})</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>IF132-B(^{b})</td>
<td>16</td>
<td>16</td>
</tr>
</tbody>
</table>

\(^{a}\): Before irradiation.  
\(^{b}\): After irradiation.

Table 5 Index variation due to air exposure.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>(\Delta n) from reference sample ((10^{-6})) 20°C at 193.4 nm</th>
<th>Uncertainty in (\Delta n) ((2\sigma) (10^{-6}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF132-A(^{a})</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>IF132-B(^{b})</td>
<td>-11</td>
<td>25</td>
</tr>
<tr>
<td>IF132-C(^{c})</td>
<td>-45</td>
<td>18</td>
</tr>
<tr>
<td>IF132-D(^{d})</td>
<td>-2</td>
<td>12</td>
</tr>
</tbody>
</table>

\(^{a}\): Original sample.  
\(^{b}\): Unexposed.  
\(^{c}\): Exposed to air.  
\(^{d}\): Stored in \(N_2\) box overnight.

Table 6 Index variation due to resist exposure.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>(\Delta n) from reference sample ((10^{-6})) 20°C at 193.4 nm</th>
<th>Uncertainty in (\Delta n) ((2\sigma) (10^{-6}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF132-A(^{a})</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td>IF132-B(^{b})</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>IF132-C(^{c})</td>
<td>-12</td>
<td>12</td>
</tr>
<tr>
<td>IF132-D(^{d})</td>
<td>-9</td>
<td>12</td>
</tr>
</tbody>
</table>

\(^{a}\): Before radiation.  
\(^{b}\): Before resist exposure.  
\(^{c}\): After resist exposure.  
\(^{d}\): After resist exposure, then sparged with \(N_2\).
fraction compared the cis-isomer. Table 7 shows the decalin isomer series results. The large differences in the index of refraction of ~0.01 are clearly due to the different molecular configurations of the two components of the mixture.

### 3.4 $\Delta n/\Delta \lambda$ values

Table 8 shows the values of $\Delta n/\Delta \lambda$ for the two immersion fluids, with water listed as well for reference. IF132 has a $\Delta n/\Delta \lambda$ value of $-2550 \times 10^{-6}$/nm and IF169 has a $\Delta n/\Delta \lambda$ value of $-2720 \times 10^{-6}$/nm at 193.4 nm, respectively, while water has a $\Delta n/\Delta \lambda$ value of $-2100 \times 10^{-6}$/nm. The values of $\Delta n/\Delta \lambda$ for immersion fluids are slightly higher than water due to the larger dispersion of these fluids compared to water mean that thermal stabilization requirements of the steppers may be more stringent than what was needed in first-generation systems. However, their refractive indices are mostly insensitive to environmental exposure and routine handling to within the uncertainty of our measurements; the only measurable changes were due to oxygen exposure and appear to be reversible. The optical properties of these fluids will have to be considered along with mechanical requirements and the availability of appropriate lens materials to assess the viability of second-generation immersion lithography.

### Acknowledgments

The authors acknowledge the assistance of Barbara French for editing the manuscript and Michael Lemon, Robert Wheland, and Sheng Peng for the sample preparations.

### References


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Roger H. French holds a PhD in materials science from MIT, where his work involved vacuum ultraviolet spectroscopy on Al₂O₃ from 80 to 800 nm. He is a Research Fellow in materials science in Central Research at the DuPont Company in Wilmington, Delaware and also an adjunct professor of materials science at the University of Pennsylvania. His research is in optical properties and electronic structure of ceramics, optical materials, and polymers. His work on new materials for optical lithography for integrated circuit fabrication has produced attenuating phase shift photomasks, photomask pellicles, semiconductor photoresists, and, most recently, lithographic immersion fluids. He also works on the origins and applications of London dispersion forces and the electronic structure and wetting of interfaces, such as intergranular and surficial films. He studies near-field optics and scattering by particulate dispersions and complex microstructures using computational solutions to Maxwell’s equations. His work has produced 20 issued patents and 135 published papers.

John H. Burnett received a PhD in physics from Harvard University in 1990, where he also did postdoctoral work. He has since been a staff scientist in the Atomic Physics Division at NIST in Gaithersburg. His principal research area has been experimental studies on the optical properties of solids and liquids, from the visible through the vacuum ultraviolet, with a recent focus on optical materials important for 193 and 157 nm lithographies.