Second Generation Fluids for 193 nm Immersion Lithography
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ABSTRACT

Water is the first generation immersion fluid for 193 nm immersion lithography. With a fluid refractive index of 1.436 and an optical absorbance of 0.01/cm at 193 nm, water immersion technology can enable optical lithography for the ITRS’ 65 nm half-pitch node. However, to achieve numerical apertures above 1.35 and to go beyond the 45 nm node, low absorbance fluids with indices higher than 1.6 are needed for the second generation of immersion lithography.

We have developed a number of Gen. 2 high index fluids for immersion lithography at 193 nm. These highly transparent fluids have 193 nm indices up to 1.67. 32 nm 1:1 line space imaging has been demonstrated using two of our Gen 2 candidate fluids, representing major advance in optical lithography.

To understand the behavior and performance of different fluid classes, we use spectral index measurements to characterize the index dispersion, coupled with Urbach absorption edge analysis, and Lorentz oscillator modeling.

1. Introduction

1.1. Roadmap For 193i Lithographic Opportunity

As the semiconductor industry advances along the ITRS, optical lithography progress enables smaller feature sizes by utilizing new technological advances. A recent transition has been the introduction of 193 nm immersion (193i) lithography to follow 193 nm dry lithography. The first generation (Gen 1) of 193i uses water as the immersion fluid, and appears to have applicability at the 65 nm and 45 nm half pitch nodes. The continued advance of 193i lithography will require the introduction of new, higher index, low absorbance fluids.

The Rayleigh equation applicable for immersion lithography, \( h_p = \frac{k_1 \lambda}{n_{IF} NA} \) (where \( h_p \) is the 1:1 half pitch feature size, \( \lambda \) is the lithographic wavelength, \( n_{IF} \) is the immersion fluid’s index of refraction at the lithographic wavelength, NA is the numerical aperture of the stepper’s lens, and \( k_1 \) is a measure of the lithographic process capability) allows one to see that the stepper NA is limited by the fluid’s index. For example with water, the upper limit of the stepper’s NA is 1.3 or 1.35. To achieve a higher NA requires a second generation immersion fluid with a higher index.

1.2. Requirements of 193 nm Immersion Litho

One can therefore consider three generations of 193i fluids to, the first generation (Gen 1) defined by water’s properties and allowing lithography to approach the 45 nm \( h_p \) node with reasonable \( k_1 \) values. To achieve 32 nm \( h_p \) imaging with a \( k_1 \) of 0.25 or 38 nm with a \( k_1 \) of 0.3, will require a second generation (Gen 2) fluid with a 193 nm index of refraction greater than 1.6, while a third generation (Gen 3) 193i fluid with a 193 nm index of refraction greater than 1.8 could enable sub 32 nm \( h_p \) feature sizes.

In addition to the fluids’ index of refraction requirements, there are two requirements for the fluids’ optical absorbance, depending on the last lens element design. As summarized in Table 1 for a flat last surface, the optical absorbance of the immersion fluid should be < 0.15/cm; if the last surface is curved, then a more stringent absorbance requirement of < 0.03/cm is needed. In addition, the index change with temperature (\( dn/dT \)) must be less than 250 ppm/K or 50 ppm/K, respectively. Finally, the viscosity and surface tension must permit good fluid handling for fast scanning, and the additional cost of ownership must be reasonable.

<table>
<thead>
<tr>
<th>Property</th>
<th>Flat last surface</th>
<th>Curved last surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption (log-base)</td>
<td>&lt; 0.15 /cm</td>
<td>&lt; 0.03 /cm</td>
</tr>
<tr>
<td>dn/dT</td>
<td>&lt; 250 ppm</td>
<td>&lt; 50 ppm</td>
</tr>
<tr>
<td>Viscosity</td>
<td>&lt; 0.003 Pas (similar as water)</td>
<td></td>
</tr>
<tr>
<td>Surface tension</td>
<td>Similar as water</td>
<td></td>
</tr>
<tr>
<td>Added COO</td>
<td>Order 1 $ / water</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Property Requirements for Generation 2 Immersion Fluids.
1.3. Approaches For Gen 2 IFs

To meet these multiple property requirements, many groups have been pursuing candidates for Gen 2 immersion fluids. Water additives is one large class being reported in the literature. For example researchers at RIT\(^2\) have reported on acids such as sulfuric and phosphoric acid as Gen 2 candidates, while researchers at Columbia\(^3\) have reported on surfactant additives to water. Also, researchers at Clemson\(^4\) have presented nanoparticle additives to water, and researchers at University of Texas Austin\(^5\) have reported on quaternary ammonium salts as water additives. In addition, researchers at Air Products\(^6\) and JSR\(^7\) have also presented results on Gen 2 fluids.

2. Methods,

2.1. VUV Spectroscopy

In this work, the index of refraction measurements were done using a prism minimum deviation technique, using both a J.A. Woollam Co. VUV-VASE® and a DUV-VASE spectroscopic ellipsometer system capable of measurement over the spectral range 140 to 1700 nm and 187 to 1100 nm respectively. The optical absorbance measurements were done using a relative transmission measurement

2.2. Index of Refraction Measurements

Spectral index of refraction measurements\(^8,9\) are performed using a liquid-filled prism cell mounted on the sample stage. The ellipsometer then determines the minimum deviation angle for light transmitted through the prism at each wavelength. The fluid refractive index, \(n_{\text{fluid}}(\lambda)\) is then given by

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

where \(\alpha\) = prism apex angle, \(\delta(\lambda)\) = measured minimum deviation angle, \(n_{\text{gas}}(\lambda)\) = index of the N\(_2\) ambient (\(N_{\text{nitrogen}} = 1.0003\) approximately. The index measurement accuracy is typically \(\sim 3 \times 10^{-4}\), even though the method can in principle be accurate to \(\sim 1 \text{ to } 10 \text{ ppm}\).

It is very useful when designing high index immersion fluids to consider the different contributions to the index of refraction at the lithographic wavelength. One finds it is useful to consider the d-line index and the spectral dispersion of the index independently, since these two terms can vary relatively independently with fluid physical properties. For example, the index of refraction of a 17.6 Megohm sample of water is shown in Figure 1, where the index of refraction at 193 nm \((n_{193})\) is shown along with the d-line index \((n_d)\) and the dispersion \(\Delta n\), where \(\Delta n\) is defined as \(\Delta n \equiv n_{193} - n_d\). From this we see that the 193 nm index of water of 1.437, consists of a d-line index of 1.334 and a dispersion of 0.103. These two contributions to the lithographic index are useful materials parameters when comparing different fluids.

2.3. Optical Absorbance Measurements

The optical absorbance of the fluid samples was determined by measuring the transmission of different thickness fluid samples using a Harrick Scientific Corp. Demountable Liquid Cell model DLC-M13, or a modified long path length cell which permitted up to 10 cm long optical path lengths in the fluid. Teflon spacers from 6 or 25 micrometer thickness, up to 10 cm thickness, were used to establish the desired path lengths and were sandwiched between two 2mm thick \(\frac{1}{2}''\) or 1” diameter CaF\(_2\) windows. The optical absorbance/cm (base 10) is then determined by
where \( T \) is the transmission and \( t \) is the thickness or path length in the fluid and \( A/cm \) is the absorbance/cm. Advantageously, if more than 2 path lengths are used then using \( T_n(\lambda) = T_0(\lambda)e^{-\alpha(\lambda)t_n} \), one can solve the resulting system of equations, and arrive at a standard deviation of the optical absorbance/cm reproducibility from the multiple measurements.

The optical absorbance of the 17.6 Megohm water sample is shown in Figure 2, where the measured absorbance is 0.101/cm with a reproducibility standard deviation of 0.009/cm. The 193 nm optical absorbance of high purity water is typically 0.01/cm, but the absorbance varies strongly with the presence of small amounts of absorbing extrinsic impurities, as must be the case here.

3. Optics of Immersion Fluids

With the two immersion fluid critical properties being index of refraction and optical absorbance at the lithographic wavelength, it is useful to have some analytical approaches to address issues which arise in these two properties, as a means to understand and optimize fluid performance.

3.1. Lorentz Oscillator Modeling

The Lorentz Oscillator \(^{10} \) (LO) is a useful tool for modeling complex optical properties. The optical properties of a Lorentz oscillator model can be solved analytically and represent an exact solution to Maxwell’s equations of light, for the response of a simple harmonic oscillator to an electromagnetic wave. Using the quantum mechanical form of the Lorentz Oscillator, and allowing for the construction of models involving multiple oscillators, one can build models and determine complex optical property responses of the model.

Consider the Lorentz Oscillator equation for the complex dielectric function \( (\varepsilon) \) as a function of photon frequency \( (\omega) \):

\[
\hat{\varepsilon}(\omega) = 1 + \frac{4\pi N e^2}{m} \sum_j \frac{f_j}{(\omega_j^2 - \omega^2) + i\Gamma_j \omega}.
\]

Here \( \Gamma \) is oscillator width, \( \omega_0 \) is oscillator frequency, \( N \) is electron density, and the \( f_j \) is the oscillator strength. The plasma frequency \( \omega_p \) is directly related to the electron density; \( \omega_p = \frac{4\pi N e^2}{m} \) and in the quantum mechanical Lorentz Oscillator model, the oscillator strengths are defined to sum to 1; \( \sum_j f_j = 1 \). Once one has the dielectric function of the LO, then one can calculate the complex index of refraction from the dielectric function as follows: \( \varepsilon_1 + i\varepsilon_2 = (n + ik)^2 \).

Then one can also calculate the absorption coefficient \( \alpha \), from

\[
A/cm = \frac{\log_{10}(T_1) - \log_{10}(T_2)}{t_2 - t_1}
\]

where

\[
\frac{\log_{10}(T_1) - \log_{10}(T_2)}{t_2 - t_1}
\]

Figure 2. Optical absorbance of 17.6 Megohm water, measured using relative transmission measurement at 3 thicknesses. The Urbach edge fit to this absorption edge is also shown along with the Urbach fit parameters.

Figure 3. The index of refraction \( n \) and extinction coefficient \( k \) of a Lorentz Oscillator Model, using three oscillators, which mimics the index and dispersion of water in the UV.
the extinction coefficient; \( \alpha = \frac{4\pi k}{\lambda} \).

We can then construct an LO model, using three oscillators, to represent low, medium and high energy bonding in the material, and adjust the plasma frequency, the oscillator energies, widths and strengths, so as to yield a model which has the same spectral index or refraction as measured for water. Such a model, mimicking the index of water, is shown in Figure 3. This model is not unique, but it is useful to demonstrate the coupled nature of the a material’s absorption and index. Also, it allows us to vary the model parameters and see how they affect the values of \( n_d \), \( n_{193} \) and \( \Delta n \), along with the coupled absorption, and the absorption edge. For example it allows us to see how a material’s density (as represented by the plasma frequency) or the absorption edge energy (as represented by the energy and width of the first LO) can be varied. It can also show how an increase in the oscillator strength of the first oscillator (\( f_1 \)) can increase the dispersion of the index of refraction.

3.2. Urbach Analysis of Absorption Edges

Urbach edge analysis is a useful way to parametrically characterize a fluid’s optical absorption edge, to distinguish intrinsic and extrinsic contributions to the absorbance.\(^{11,12}\) Urbach\(^3\) originally observed that a material’s optical absorption, for energies below the fundamental optical absorption edge, is exponential in nature, and can be characterized by

\[
\alpha(E) = e^{-\frac{|E-E_0|}{W}}
\]

where the absorption coefficient \( \alpha \) as a function E, is characterized by the Urbach edge energy (\( E_0 \)) and the Urbach width (\( W \)), which is related to the slope of the Urbach edge.

In Figure 2, we show the Urbach edge fit to the optical absorption edge of 17.6 Megohm water. One can see the Urbach edge fits underneath the measured absorption edge for energies below the fundamental absorption edge, and we can characterize the Urbach edge position to be 185.2 nm (using the \( \text{nm} \div \text{eV} \) conversion \( \lambda(\text{nm}) = 1239.8/\text{E(eV)} \)) and the Urbach width is 3.5 nm. We can also compare the absorption coefficient at 193nm for the measured absorbance (0.101/cm) and the Urbach absorption edge (0.099/cm). The optical absorption of clean water at 193nm is 0.01/cm, and so in this case the broad, diffuse nature of the extrinsic absorbers does not allow the Urbach edge fit to discriminate the extrinsic contributions from the intrinsic contributions to the optical absorption.

4. Chemistry of IF's For Gen 2

The need for higher index lithographic immersion fluids, to serve as the 2\(^{nd} \) generation of fluids replacing water, has produced a large amount of research activity focused on identify high index, low absorbance fluids. We will consider these in three groupings: aqueous, organic and (in section 5) the candidate immersion fluids we have been developing.

When considering immersion fluid families, it is useful to develop an optical property map, showing both the
lithographic index and the optical absorbance at 193nm. Figure 4 shows the index/absorbance map for various fluids, with the initial standard being the Gen 1 fluid, Water.

4.1. Aqueous Candidates

Tetraethylorthosilicate (TEOS) is one possible fluid and as shown in Figure 4, it has an index of refraction on the order of 1.5, and therefore does not achieve the $n_{193}=1.6$ criteria for a Gen 2 fluid. RIT has presented work at this conference on acids, such as concentrated sulfuric and phosphoric acids, and in this case the indices we measure are in the range or 1.5 to1.55. Other groups are looking at surfactants (Columbia) and quaternary ammonium salts (UT Austin); in our measurements, these classes have indices below 1.5 at 193 nm.

4.2. Optics of Mixtures

In the case of aqueous blends of acids, salts, or surfactants, it is useful to consider the possible impact of mixtures on the index of refraction at 193 nm using a Lorentz Oscillator model to simulate the possible mixture optics. In Figure 5, we show two different 3 LO models, one which mimics the index and dispersion in the visible and UV range of water, and the other which mimics the index and dispersion of TEOS. The difference in the models is in the energy and broadening of the oscillators, and these changes lead to differences in the complex index of refraction. We can use these Lorentz oscillator models, and by adding the oscillators in different manners, we can develop two models which represent different possible mixture types of the dopant in water. We will assume a 50:50 ratio of water and dopant.

In Figure 6 we show the spectral index of refraction for the water and the dopant LO model, and then consider the case of a non-interacting mixture, and a second mixture model in which there is an interaction between the water and the dopant.

In the non-interacting mixture, we can simply sum the oscillators of the water and dopant materials, while reducing the oscillator strength of each oscillator to represent its 50% contribution to the new “mixture”. This non-interacting “additive” mixture represents the case where the water and dopant species do not modify each other’s properties, and where the 50:50 mixture shows an index of refraction which is halfway between that of the two components. In this case, the dopant’s higher index of refraction is reduced in direct proportion to the concentration of the lower index component, water.

While it gives rise to the simple rule of mixture behavior, the case of a non-interacting mixture may well represent a special, and even unusual case. The more general case is one where the dopant shows some level of interaction with the water, and they each undergo some modification, be it simple complexation or more fundamental chemical reaction. In this case, one expects that the different LOs in the resulting mixture are modified from the component materials. To represent this case, we take the 6 different oscillators present in the two LO models for water and dopant, and produce a mixture model consisting of three oscillators. These oscillators have energies intermediate between those of water and dopant, and widths which are determined by the

Figure 6. Lorentz Oscillator models, representing 50:50 mixtures of Water and a TEOS like dopant, based on two approaches, a non-interacting (additive) mixture and an interacting (broadening) mixture. Note the changes in the $n_d$ and $n_{193}$, and the dispersion for the two different models.

Figure 7. Optical absorption edge, and Urbach edge for IF132 showing a low absorbance Gen 2 immersion fluid.
sum of the width of the component materials and the energy difference of the component oscillators. We call this an interacting “broadening” mixture model, since the interactions between the two components lead to a broadening of the oscillators in the mixture. In this case, one can see a radical change in the model’s index of refraction; the behavior is no long rule-of-mixtures like, but instead shows a reduced d-line index, and an index of refraction below water at 193 nm. So unlike the rule of mixtures where one gets a refractive index intermediate between that of the two components, in the interacting broadening model the index of the mixture is actually less that the indices of either component at 193 nm. This situation arises because the broadening while not changing 

LO modeling thus suggests that mixtures may very well show counterintuitive changes in refractive index when the components of the mixture interact chemically or physically. This is because the index of refraction consists of both 

4.3. Hydrocarbon Candidates

Beyond the materials classes mentioned above, it is also of interest to consider the optical properties of hydrocarbons, such as alkanes. In Figure 4 the index of refraction for four linear and cyclic alkanes is shown, and these fluids have indices above 1.55.

5. High Index, 193 nm, Gen 2 Immersion Fluids

We have developed a large number of Gen 2 candidate fluids which exceed the index of refraction requirement, and some also meet the optical absorbance requirement.

5.1. Low Absorbance Fluids

In Figure 7 we show the optical absorption edge of IF132, along with an Urbach edge fit. This fluid has an absorbance of 0.083/cm. The Urbach edge position is 187.1 nm, as compared to water at 185.2 nm, and the Urbach width is 2.3 nm as compared to the Urbach width of water shown in Figure 2 of 3.5 nm.

5.2. High Index Fluids

In Figure 8 we compare the spectral index of refraction of water with that of a Gen2 candidate, IF175. Here we see that IF175 has a d-line index of 1.497 compared to water’s index of 1.33. The dispersion of IF175 is 0.165, which is much larger than the dispersion of 0.103 for water, and from this the index of refraction of IF175 at 193 nm is 1.664, a substantial improvement over water’s index of 1.437.

Figure 8. Spectral index of refraction of IF175 compared to the index of refraction of water. Note IF175’s increased nd, dispersion Δn and n193.

Figure 9. Immersion interference imaging showing 32 nm 1:1 Line/Spaces using IF131.
6. Printing Performance of Gen2 IF

These Gen 2 immersion fluids enable the printing of 32 nm 1:1 Line/Space arrays. From Immersion Interference Lithography results of Harry Sewell of ASML shown in Figure 9 using IF131, and in Figure 10 using IF132, we see that good imaging at a $k_1$ of 0.25 is possible with these Gen 2 immersion fluids. The line edge roughness visible in these images is a function of the resists’ performance, and is not attributable to the immersion fluid. These images were taken using a topcoat to reduce environmental interactions.

7. Conclusions

We have developed a number of Gen. 2 high index fluids for immersion lithography at 193 nm. These highly transparent fluids have 193 nm indices up to 1.67. 32 nm 1:1 line space imaging has been demonstrated using two of our Gen 2 candidate fluids, representing a major advance in optical lithography.

To understand the behavior and performance of different fluid classes, we use spectral index measurements to characterize the index dispersion, coupled with Urbach optical absorption edge analysis, and Lorentz oscillator modeling.

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3 Columbia, see this conference, SPIE Microlithography, 5753-61, (2005).

4 Clemson, see this conference, SPIE Microlithography, 5753-98, (2005).

5 UT Austin, see this conference, SPIE Microlithography, 5753-97, (2005).


7 JSR, see this conference, SPIE Microlithography, 5753-3, (2005).


