High Refractive Index Immersion Fluids for 193nm Immersion Lithography

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ABSTRACT

For the next-generation immersion lithography technology, there is a growing interest in the immersion fluids having a refractive index larger than 1.5 and low absorbance at 193nm wavelength. In this paper, we report our effort in identifying new immersion fluid candidates. The absolute refractive index values and thermo-optic coefficients, d***n***/d**T**, were measured with 1×10^{-4} and 1×10^{-5} accuracy respectively at 193nm wavelength. The results showed promising candidates having refractive index ranging from 1.5 to 1.65 with low absorbance at 193nm wavelength. Preliminary imaging results with a new immersion fluid gave good 65nm Line/Space patterns. However, the minimum exposure time of 20sec is about ten times as needed for water, indicating the need to further reduce the absorbance of the immersion fluid.

Keywords: immersion fluid, high refractive index, immersion lithography, absorbance, 193nm, Hilger-Chance

1. INTRODUCTION

The desire to develop immersion systems is growing more acute because the ability to achieve resolution improvements via conventional means, such as wavelength reduction, is increasingly difficult. In addition, numerical apertures (*NA)* produced by lithographic methods using air between the wafer and the last optical element of the lens is approaching the theoretical limit. Immersion lithography has emerged as a cost-effective extension of current optical lithography technology with improved depth of focus (*DOF*) and resolution. The premise behind this technique is to increase the refractive index (***n***) of the space between bottom lens and wafer by filling with a high-index fluid, which also has to be transparent at the exposure wavelength. The requirements for 193nm immersion fluids include transparency at the operating wavelengths, high refractive index, ***n*** and low viscosity. Additional attributes are good wetting behavior on resists or topcoats and optical element surfaces, low foaming characteristics to minimize the formation of nanobubbles on various surfaces, and chemical compatibility with the photoresist and the lens element. For 193nm immersion tools with *NA* less than 1, water (***n*** =1.44) has been selected as the best immersion medium[1]. Water is the most transparent fluid measured[2] with absorption coefficient, α, as low as 0.036cm^{-1}.

There is now a consensus that for 193nm immersion lithography (193*i*) water will be the most likely candidate for 65nm and 45nm device nodes bridging the gap between "dry" or conventional 193nm lithography and EUV lithography. For a given feature being printed and a given *NA*, immersion lithography will provide a greater depth of focus (*DOF*). It is widely appreciated that the increase in *DOF* provided by immersion increases the total process window available for manufacturing (with the potential to translate into better device yield for the most advanced systems)[3]. Subsequently there is a great amount of research to try to increase *NA* further into the hyper-*NA* region, ie., *NA* greater than 1 by using higher refractive index (RI) fluids (***n*** > 1.44). The industry sees higher RI fluids as the next step to reach 32nm node and possibly push out EUV lithography. These higher RI immersion fluids also need to be compatible with 193nm immersion lithographic systems.

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It was reported earlier that under certain conditions several immersion fluids minimize the formation of micro- and nanobubbles[4]. However, to our knowledge, higher refractive index fluids which meet the all the criteria have not been previously reported. In this paper, several examples of higher RI immersion fluids are presented, along with contact angle measurements, which show improved wetting on photoresists, and UV Absorption data at 193nm and immersion lithography patterning images.

2. EXPERIMENTAL

Refractive Index at 193 nm

A VUV refractometer is used to rapidly survey the absolute refractive index, $\boldsymbol{n}$, of immersion fluids at 193 nm wavelength. The experimental setup used is a VUV Hilger-Chance refractometer, which measures deviation of the laser beam through an inverted prism fluid cell. This Hilger-Chance refractometer with stringent temperature control (± 0.01 °C) allowed high-accuracy measurements ($\sigma \sim 10^{-4}$) of $\boldsymbol{n}$ and $d\boldsymbol{n}/d\boldsymbol{T}$. Before measurements with the Hilger-Chance refractometer, the fluid samples are allowed to come to equilibrium at the desired temperature. The fluid samples were placed in a V-Groove fused silica cell which is temperature-controlled and sealed from the atmosphere. In addition to temperature, humidity and pressure of the air are also monitored during the course of the measurements. The detector used is a Si photodiode.

UV Absorption at 193nm

The UV absorbance of immersion fluids was characterized using a Perkin-Elmer double beam UV Spectrometer. The measurements were made in the wavelength range of 180-210 nm under ambient temperatures and atmospheric conditions. All measurements were made in a quartz crystal curvette of path length 1 cm.

Contact Angle Measurements

A commercial acrylate type 193nm photoresist was coated onto untreated 3" or 4" silicon wafers for contact angle measurements. The contact angles of immersion fluids were measured with a G10/DSA10 Kruss drop shape analyzer using the Sessile drop method. A high-speed camera captured the spreading of the droplet at a speed of 2 frames per second for 30 seconds and the contact angle was measured from the captured droplet image. The data presented in this paper are these averages of 3 drops, with the typical reproducibility for 3 drops estimated to be $\pm 1.5^{o}$.

Imaging 65nm Dense lines with a 193 nm Interferometer

Immersion fluids were tested on a 193nm two-beam R&D interferometer modified to hold a 200 mm diameter silicon wafer contacting a reservoir with the fluids of interest. This research tool comprised of a two-beam diffraction plate (splitter) which allowed sin (θ) and hence resolution to be set by adjusting the position and angle of the diffraction mirrors. The two first order beams form an interference pattern with a pitch of 130nm in the photoresist coating of the silicon wafer. The system can facilitate resolution (half pitch) < 65nm line/space at 193nm wavelength. In this work, 65nm line/space pattern was imaged using selected immersion fluids.

3. RESULTS AND DISCUSSION

Refractive Index , d*n*/dT and UV Absorbance Measurements at 193 nm

Early experimental work on immersion fluids by Switkes et. al[5] proposed using water for 193nm and perfluoro-polyether (PFPE) materials for 157nm lithography. Table 1 lists one example of proposed specifications[6] of any potential immersion fluid compared to that of water.

Table. 1. Physical Parameters Specified for Immersion Fluid Candidates[6].

Parameter	Water @ 193nm	Higher refractive index Immersion Fluid @ 193nm
Absorbance (base 10)	0.036/cm	≤ 0.40/cm
Refractive index, *n*	~1.43	≥ 1.50
d*n*/dT	~100 ppm/K	≤ 300 ppm/K

The absorption coefficient of water would allow working distances >6mm for 95% Transmittance, much larger than will be required in actual tools. For higher RI immersion fluids the absorption coefficient is ideally[6] α <0.40 cm^{-1} for 1mm working distance which corresponds to 91% Transmittance. NIST has reported[7] the ***n*** (λ) value for water with precision better than 5 decimals (1.43664 ± 0.00002, 21.5 ^oC, 193.39nm), and d***n***/d**T** value of -1.0×10^{-4} K^{-1}. The d***n***/d**T** value is used to evaluate the thermal aberration in the water/fluid.

Our measurements of refractive index identified several immersion fluids, aqueous-based as well as non-aqueous based, with refractive indexes ranging from 1.45 to 1.65, significantly higher than that of water at 1.43, as shown in Table 2. The UV Absorption spectra of some of the higher refractive index immersion fluids are shown in Figure 1. It can be seen that several candidates show sufficiently low absorption at 193nm wavelength of <2.0 cm^{-1}. However, as noted in Table 2 and Figure 1, the fluids which gave the highest refractive indices also have high UV absorbance. A critical analysis of the structure-property relationship of these immersion fluids show that no simple correlations for RI and UV absorbance can be made. The Lorentz-Lorenz formula for refractive index of a condensed material provides a convenient framework for thinking about possible immersion fluids, where refractive index is found to depend not only on the molar density of the material but also on the molecular polarizability of the molecule[8]. An attempt to increase refractive index by increasing polarizability, often inevitably leads to an increase in absorption. This technical challenge is outlined fundamentally by the Kramers-Kronig dispersion relations that correlate the absorbance and the refractive index of molecules[9]. As such, the design of high refractive index, low absorption immersion fluids requires the consideration of the interatomic bonding and optical properties of materials. Ongoing fundamental analysis by molecular modeling is being explored for designing high refractive index, low absorbance immersion fluids.

Despite this technical challenge, several good candidates were obtained. Three candidate immersion fluids, IF 3, IF 4 and IF 5, that met the requirement for refractive index (>1.50), light absorption (<2.0cm^{-1}) and index homogeneity, were selected for further testing and imaging. An absorption coefficient value of 2.0 cm^{-1} corresponds to 80% Transmittance at 0.5 mm working distance.

The changes in the refractive index with temperature, d***n***/d**T**, and absorbance at 193nm are also shown in Table 2. It can be seen that several candidates gave d***n***/d**T** comparable to that of water with the exception of IF 2 which was the only immersion fluid tested that gave a positive d***n***/d**T**. The change in refractive index with temperature is inverse to that of water. The use of an immersion fluid with antagonistic refractive index/temperature (d***n***/d**T**) characteristics can also be used to increase the resolution.

Table 2. Immersion Fluids with Refractive Indices and Absorbance at 193nm and 21.5 °C.

Immersion Fluids	[a]Absorbance /cm @ 193nm	*n* @ 193nm (21.5 °C)	d*n*/dT (°C)
H_2O (HPLC)	0.0412	1.4366	-0.0001
IF 1	0.317	1.4450	-0.00011
IF 2	5.397	1.4556	0.000079
IF 3	0.940	1.5010	-0.00025
IF 4	1.939	1.5154	-
IF 5	1.144	1.5573	-
IF 6	>6	1.5606	
IF 7	2.015	1.5755	-0.00043
IF 8	>6	1.6441	-0.00073

[a] **Absorbance ≡ A/l = α . c**

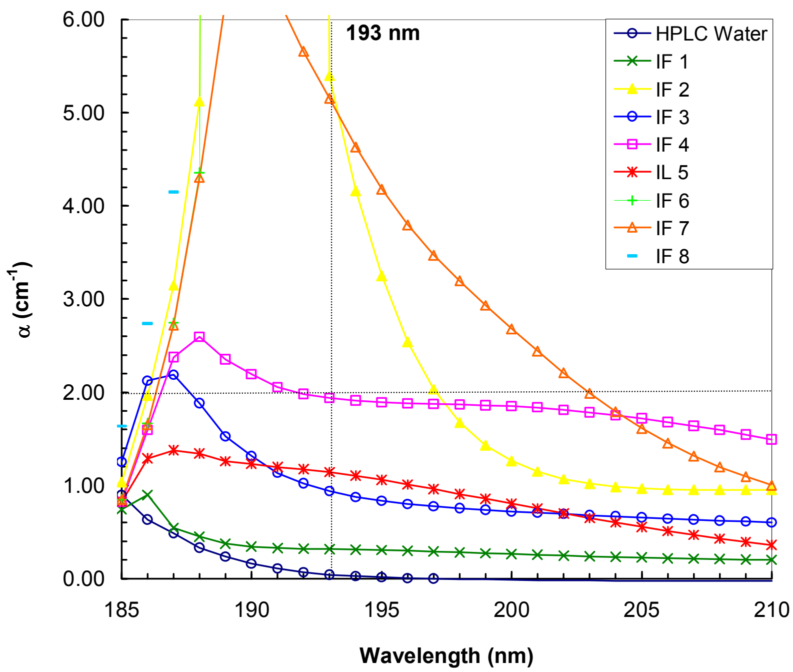


Figure 1. UV Absorption Spectra of High Refractive Index Immersion Fluids.

Wetting studies of Immersion Fluids

The flow dynamics of immersion fluids can be characterized by their wetting properties on photoresist surfaces. The effective wetting of the surface of the photoresist by the immersion fluid is crucial to minimize voids or cavities which may lead to bubbles or splashing. Effective wetting of the photoresist surface by the immersion fluid is inherently tied to the surface energy properties of the photoresist polymer. Typical 193nm photoresists are acrylate based polymers which wet well with aqueous fluids. However, recent research has shown that significant amounts of photoacid generator (PAG) leaching occurs during immersion lithography when water is used as the immersion fluid[10]. As such, several researchers have adopted the use of top-coats as a barrier to minimize chemical interactions and PAG leaching during immersion lithography. These top-coats often contain fluorine, which gives an extremely low energy surface that does not wet well with aqueous solutions.

The results shown in Figure 2 illustrate a wide range of contact angles. Some higher refractive index immersion fluids gave relatively high contact angles, comparable to that of water at 70^{o}. Other immersion fluids gave very low contact angle at 15^{o} and 8^{o} for immersion fluid, IF 6 and IF 5, respectively. The results show that IF 5 gave the lowest contact angle. In fact, there was instantaneous complete wetting on the surface within fractions of a second.

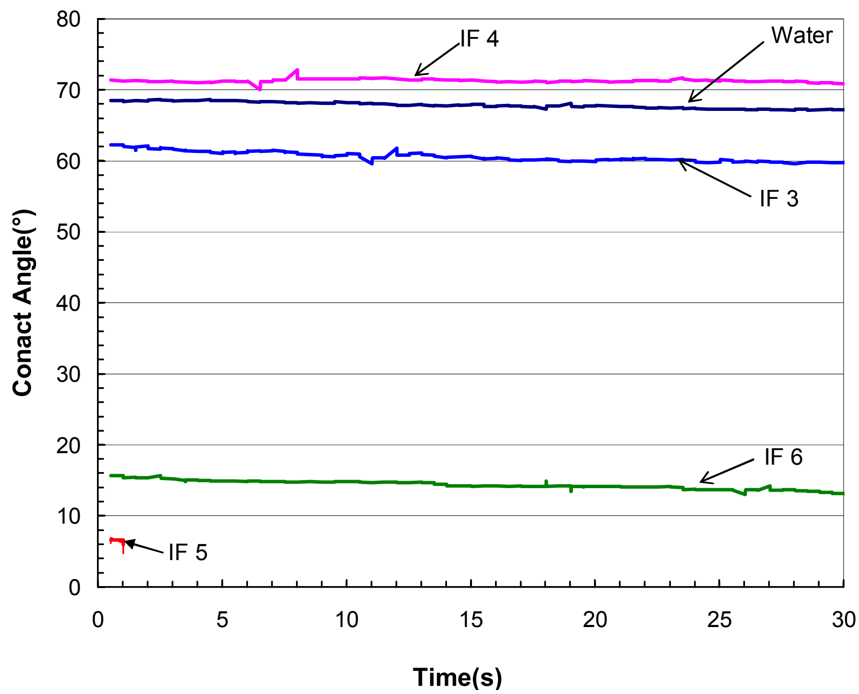


Figure 2. Dynamic Contact Angle Measurements of Immersion Fluids on unexposed 193nm Photoresist.

Additional screening of higher refractive index immersion fluids must be conducted to determine what contact angles will demonstrate the most effective and efficient wetting and de-wetting behavior on a variety of 193nm photoresists and top-coats.

Immersion Lithography Patterning

Three candidate immersion fluids, IF 3, IF 4 and IF 5, met the requirement for refractive index (>1.50), light absorption (<2.0cm^{-1}) and index homogeneity, shown in the previous sections were selected to image 65nm dense L/S using a 193nm interferometer. These refractive index and UV absorbance values were shown in Table 2.

The immersion fluids were initially screened for their interaction with a 193nm photoresist and several base-developable topcoat and one non-base developable (solvent developable) top-coat. The criterion for passing the interaction testing is primarily determined by the ability of the fluid to form a drop on the photoresist or top-coat (high contact angle). This criterion is in contrast to what is required for a commercial scanner because the bench-top R&D interferometer is designed such that the wafer is mounted upside down (above the fluid cell), so the less the fluid wets the photoresist, the more likely will the drop stay on the surface and not spread by capillary action to the edge of the wafer.

Two immersion fluid candidates met all compatibility and handling requirements with no observable interactions on the resist/top-coat and demonstrated excellent or good drop height. IF 3 was evaluated with the 193nm photoresist and a base developable top-coat and IF 5 was evaluated with the 193nm photoresist and non-base developable top-coat.

With IF 5, good 65nm Line/Space patterns were obtained. Top-down and cross-sectional SEM images are shown in Figures 3 and 4 respectively. The top-down SEM images shown in Figure 3 have low contrast but these were comparable to that of distilled water (not shown). However, the minimum exposure time of 20sec is about ten times that needed for water, indicating the need to further reduce the absorbance of immersion fluid. While initially 65 line/space were imaged, 45 line/space will be made in the future. Any improvements in *DOF* and defectivity will be measured with an immersion scanner as progress is made with higher refractive index and lower absorbance fluids.

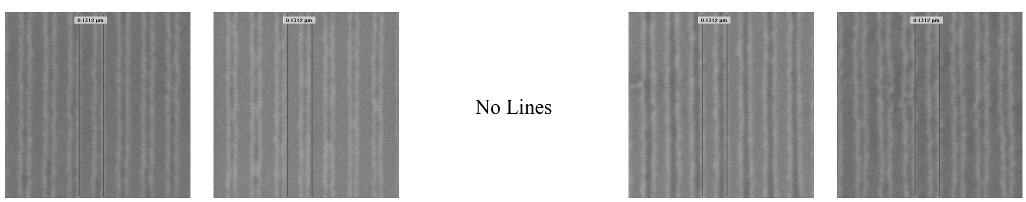
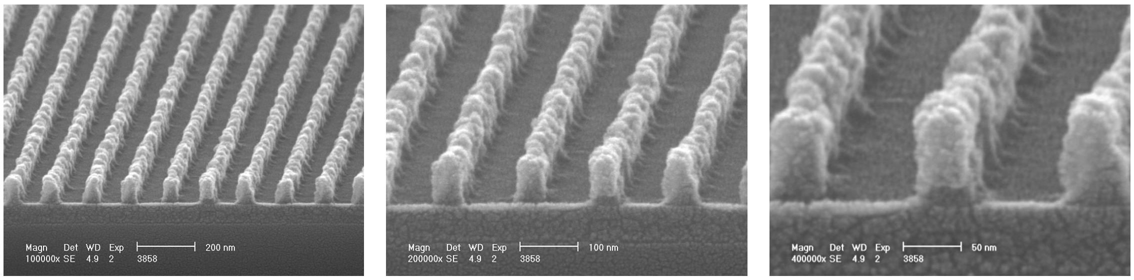


Fig. 3. Exposure result with immersion fluid, IF 5 and a non-base developable topcoat, showing top-down SEM image. Targeted CD = 65nm line/space (1:1). Minimum exposure time of 20 sec compares to water at 2 sec.

193nm Immersion Exposure, 65 nm Line/Space



Resist (1125 Å), ARC (850 Å), Topcoat (380 Å)

Fig. 4. Exposure result with IF 5 and a non-base developable topcoat, showing cross-sectional SEM image. Targeted CD = 65nm line/space (1:1).

4. CONCLUSIONS

Significant progress has been made in developing new immersion fluids having high refractive index, ***n***, low absorption and good wetting on the photoresist for 193nm immersion lithography. Several promising new immersion fluids were identified with refractive indices ranging from 1.55 to 1.65, significantly higher than that of water at 1.43. The UV absorbance at 193nm of these immersion fluids is lower than 2.0 cm^{-1}; however, further improvements are still needed to get the absorbance below 0.40cm^{-1}. The dependence of refractive index on molecular polarizbility and its correlation with the absorbance of molecules at various wavelengths is being explored by molecular modeling. This understanding will be used to optimize immersion fluid formulations to further enhance the refractive index and minimize the absorbance at 193nm. It was also demonstrated that several higher refractive index immersion fluids tested wet the surface of photoresists, while others gave comparable wetting to that of water. Preliminary imaging of 65nm dense lines using these higher refractive index immersion fluids demonstrates 193nm irradiation stability during patterning. Further testing of the best immersion fluids to obtain data on *DOF* improvements, throughput and defectivity using an immersion scanner will be made.

5. ACKNOWLEDGEMENTS

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