Immersion Fluid Refractive Indices Using Prism Minimum Deviation Techniques

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ABSTRACT

Immersion fluids for 157 nm and 193 nm immersion lithography have been measured over the spectral range from 156 nm to 1700 nm in a nitrogen purged environment. The refractive index n and k of several candidate fluids have been measured using the prism minimum deviation technique implemented on a commercial Variable Angle Spectroscopic Ellipsometer (VASE®) system. For measurement the liquids were contained in a triangular prism cell made with fused silica windows. The refractive index of high-purity water at 21.5° C measured over the spectral range 185 nm to 500 nm. was checked against values measured on high accuracy prism minimum deviation equipment by NIST and agreement with NIST has been found to be good. The refractive index at a nominal temperature of 32°C for four fluorinated fluids in the range of n=1.308 to 1.325 at 157 nm are also reported. It was found to be extremely important to correct for temperature differences among different instruments using the thermo-optic coefficient of each liquid. The 157 nm results on fluorinated fluids are compared with measurements at NIST using a VUV Hilger-Chance Refractometer, which measured both the refractive index and the thermo-optic coefficient. In all cases results agree well.

Keywords: Index of Refraction, Immersion Fluid, Immersion Lithography, 157 nm Lithography, 193 nm Lithography

1. INTRODUCTION

The development of new immersion fluids to enable immersion lithography at different lithographic wavelengths[1], requires the ability to screen novel fluids for their refractive properties, such as the refractive index. The refractive index of immersion fluids can now be measured on J.A. Woollam VASE® and VUV-VASE® spectroscopic ellipsometers. This technique is well suited for immersion fluid research and can be implemented on existing Woollam VASE® or VUV-VASE® instruments. Both n and k can be measured simultaneously and at any wavelength over the spectral range 156 nm to 1700 nm in a nitrogen purged environment.

2. PRISM MINIMUM DEVIATION METHOD

Accurate refractive index values at 193-nm and 157-nm for solids have been demonstrated using the minimum deviation method.[2,3] The minimum deviation method is commonly used to determine the refractive index of solid materials. A light beam of wavelength λ passes through a prism with a known apex angle α. By orienting the prism so that the light travels symmetrically through the prism, the deviation angle δ is at a minimum. If n_{gas} is the index of the surrounding ambient, then the material index n_{mat} is given by equation 1.

$$n_{mat}(\lambda) = \frac{\sin\left[\frac{\alpha+\delta(\lambda)}{2}\right]}{\sin\left(\frac{\alpha}{2}\right)} n_{gas}(\lambda) \qquad \text{Equation (1)}$$

The prism minimum deviation technique can be used to measure the refractive index of (semi)transparent liquids by introducing the liquid into a hollow prism as shown in Figure 1. The window refraction effects cancel out when the windows have exactly parallel surfaces, and equation (1) is still valid with n_{mat} now representing the liquid. The prism minimum deviation method is a refractive technique measuring a transmitted light beam, thus requiring both

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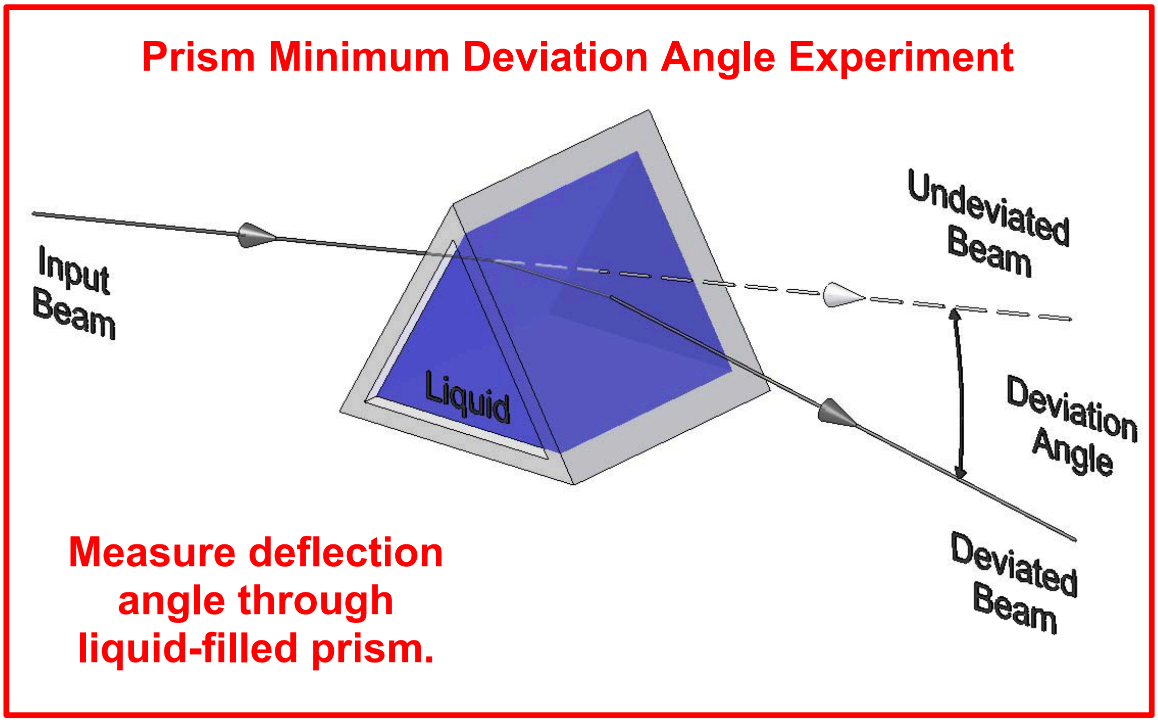

Figure 1. Prism minimum deviation measurement. Fluid is placed in a hollow prism and the deviation angle of the refracted beam is measured at different wavelengths. The measured deviation angle gives a measurement of the fluid refractive index.

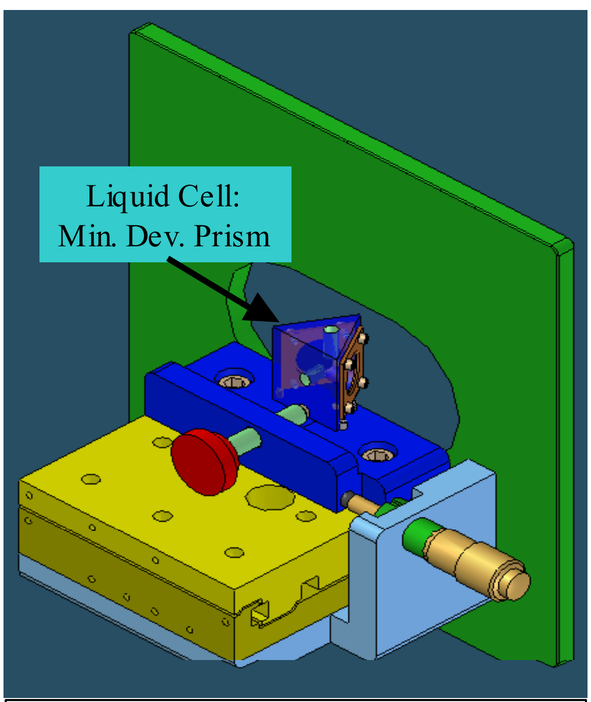

Figure 2. Liquid cell for minimum deviation measurements on the VUV-Vase sample stage.

the prism cell windows and the liquid to be (semi)transparent at the measured wavelength.

3. EXPERIMENT

This work implements the minimum deviation method using a liquid-filled prism cell on a commercial variable angle spectroscopic ellipsometer (VASE®) instrument capable of operation over the spectral range 140 nm to1700 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 the spectral dispersion of the index of refraction.

For measurement, the 60^o equilateral liquid prism was mounted on a VASE® ellipsometer with an automated Θ-2Θ angle-of-incidence stage (computer controlled, stepper motor driven). The prism was mounted on the sample stage as shown in Figure 2. The sample rotation stage (Θ) and the detector arm rotation stage (2Θ) were controlled separately during the measurement. The target wavelength λ was selected from the VUV to the near infrared (NIR) using a monochromator. For a given wavelength and incident angle, the detector arm is swept through a range of angles including the expected transmission angle in order to accurately determine the transmission angle. This process is repeated for a range of incident angles which includes the expected minimum deviation angle. Once the minimum deviation angle has been determined, the index $n_{mat}(\lambda)$ was determined by equation (1).

Measurements into the vacuum ultraviolet (VUV) for investigation around 157-nm are possible by using appropriate (semi)transparent window materials such as CaF_2 and enclosing the system in either a purged or evacuated chamber. In this work the entire optical system was enclosed in a continuous purge of dry nitrogen. The purged environment also prevents contamination of the fluid by water and oxygen which can cause variations in the fluid index (n) or extinction coefficient (k). VUV measurements were performed at a nominal temperature of 32° C. The measured spectral range could be extended further into the vacuum ultraviolet down to 140 nm by constructing the prism cell from more transparent window materials, such as CaF2.

4. RESULTS AND DISCUSSSION

4.1 Index of Refraction of Water: Confirmation of Methods

Burnett et *al*. have applied the prism minimum deviation method to measurements of water for use in 193 nm immersion applications.[4] We therefore used water as a test of our minimum deviation prism methods and the Figure 3 shows the refractive index of high-purity water at 21.5° C measured over the spectral range 185 nm to 500 nm. The water results agree very well with previous accurate values published by Burnett.

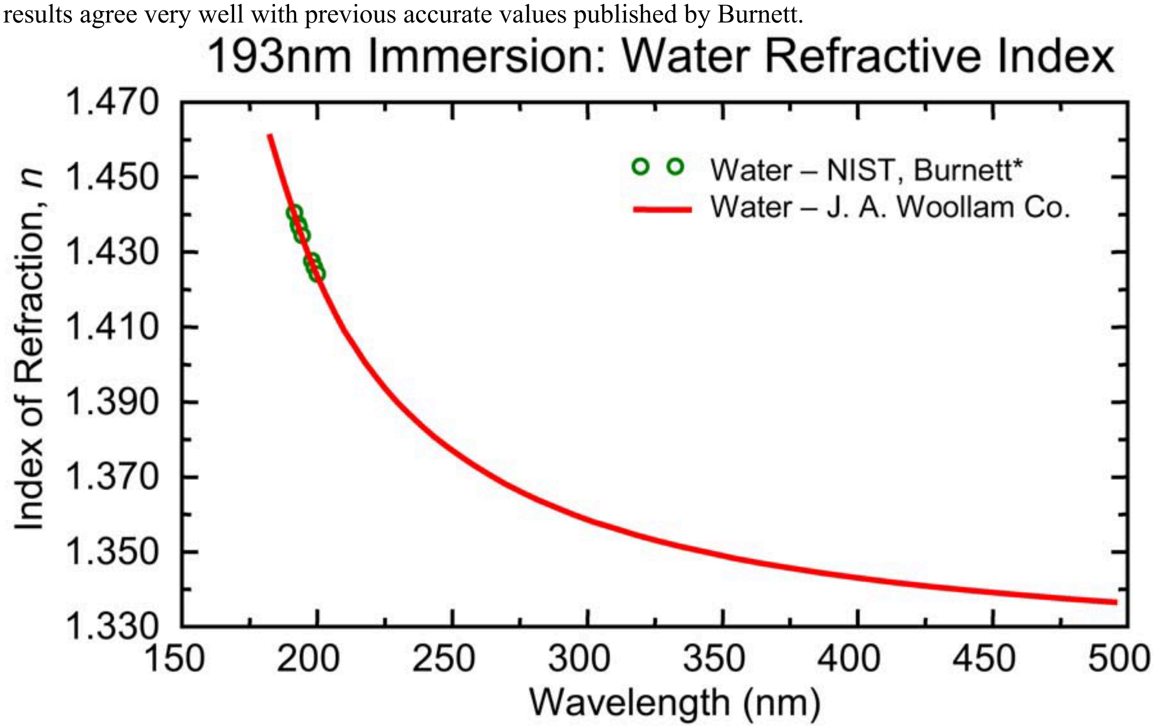

Figure 3. Refractive index versus wavelength of water over the spectral range 185 nm to 500 nm. Reference values from Burnett [4] are also shown.

4.2. Index of Refraction of Four Fluorinated Fluids

The spectral dispersion of the refractive index for four fluorinated liquids is shown in Figure 4. The indices are in the range of n=1.308 to 1.325 at 157 nm. These measurements were performed at a nominal temperature of 32° C. It was found to be extremely important to correct for temperature differences among different instruments using the thermo-optic coefficient of each liquid. These minimum deviation VASE® results for fluorinated fluids were compared to measurements of the refractive properties of three of the fluids done at NIST using a different optical geometry, referred to as the VUV Hilger-Chance Refractometer[5], in which the fluid is held in a v-groove and the angular deviation of the light is measured. The accuracy of these VUV Hilger-Chance Refractometer 157 nm results is 1×10^{-4}. This method was performed with the fluids at 21.5C, and both the index of refraction and the thermo-optic coefficient (dn/dT) were determined and are reported in Table 1. Also in Table 1 we calculate the indices of the three fluids at 32^{o}C for comparison to the minimum deviation VASE® results. For these three fluids the estimated uncertainty of the measurement is 2.3 x 10^{-3} by calculating the root mean square deviation of the Vase measurements from the VUV Hilger-Chance measurements at 32°C. The minimum deviation VASE® results can be further improved through understanding the effects of alignment and calibration on the results.

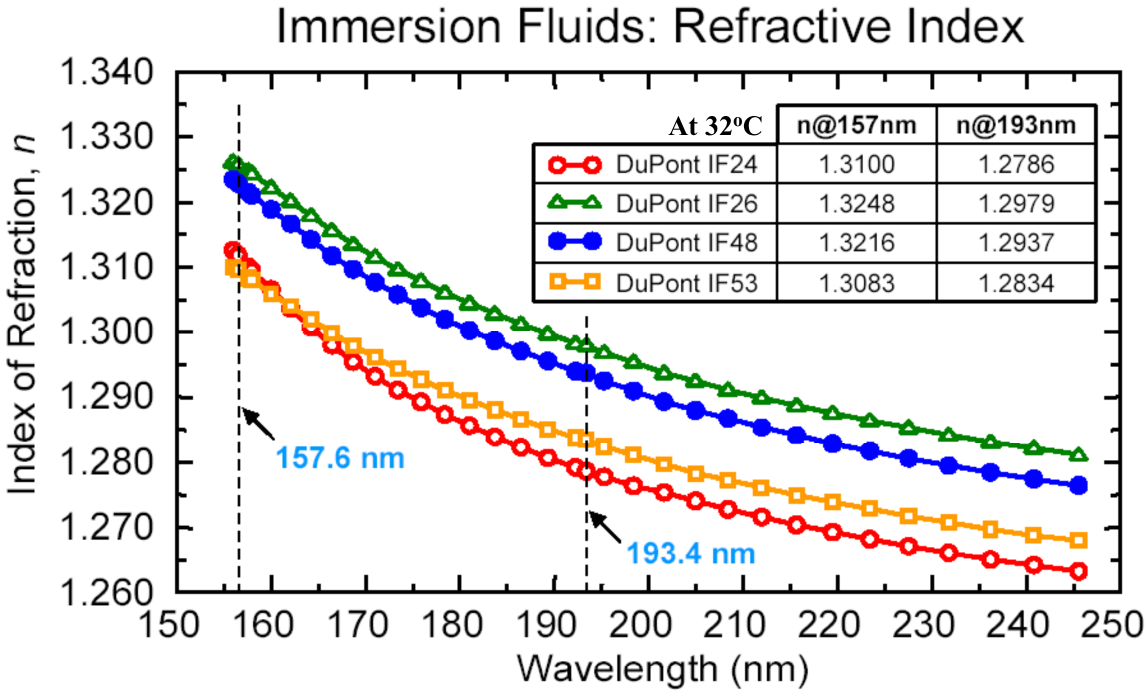

Figure 4. Refractive index n of four DuPont 157 nm immersion fluids at 32° C measured by the prism minimum deviation angle method. Measurements were made using a Woollam VUV-VASE® ellipsometer. Results for both 157 nm and 193 nm are shown. Measurements were performed at nominal temperature of 32° C

Table 1. Refractive properties of three fluorinated fluids at 157 nm, with comparison to the 193nm properties of water.[6] These results were determined using a VUV Hilger-Chance Refractometer.

Sample	***n*** (21.5 °C)	**d*n*/d*T* (°C)** (21.5 °C)	Calculated Index at 32 °C
IF24 (157 nm)	1.315,62 ± 1 × 10^{-4}	-5.83 × 10^{-4} / °C	1.3095
IF26 (157 nm)	1.329,46 ± 1 × 10^{-4}	-7.63 × 10^{-4} / °C	1.32145
IF48 (157 nm)	1.326,34 ± 1 × 10^{-4}	-6.45 × 10^{-4} / °C	1.31957
Water (193 mm)	1.436,62 ± 2 × 10^{-5}	-1.00 × 10^{-4} / °C	1.43557

4.3. Extinction Coefficient Determined During Minimum Deviation Prism Measurement

The minimum deviation prism measurement also permits the measurement of the extinction coefficient, due to the tapered nature of the 60° equilateral prism used. By a simple z translation of the liquid cell perpendicular to the incident light beam, the thickness of the optical path in the fluid varies, and this variation can be analyzed to determine the extinction coefficient by a relative transmission approach. These results are limited due to the limited range of optical path lengths accessible in the prism. The extinction coefficients determined for the three fluorinated fluids in the VUV are shown in Figure 5. We have also determined the absorbance / cm (base 10) of these samples using the relative transmission method with multiple path lengths in Harrick Liquid Cells and summarize these results in Table 2. In these independent absorbance measurements we typically measure three optical path lengths, and choose the path lengths so that they are each 3 times the shorter path length, thereby assuring a substantial change in the transmission for each optical path length. At 157 nm, we convert the absorbance /cm (base 10) to the absorption coefficient (base e) and then to the extinction coefficient, where the absorption coefficient $\alpha = 4\pi k/\lambda$. Comparing the results of the two methods the estimated uncertainty of this measurement of the extinction coefficient k is 3 x 10^{-6}. Another contribution to this variability probably arises from variations in the sample handling and possible sample contamination in these preliminary measurements.

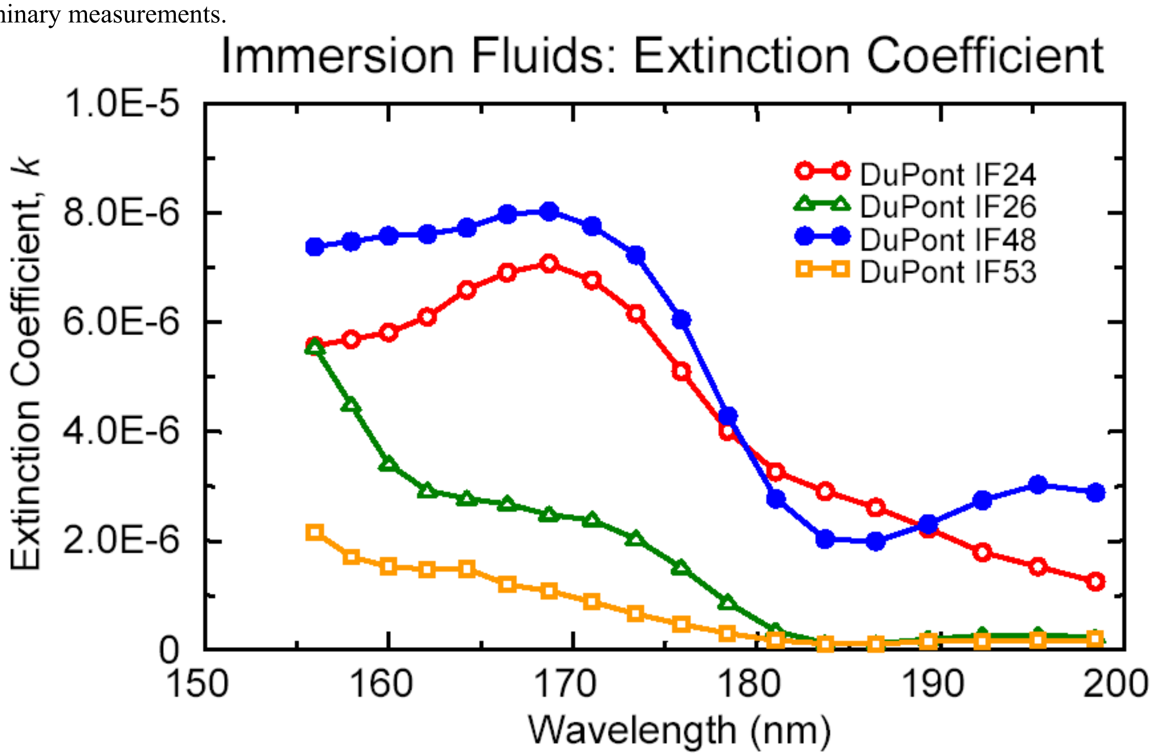

Figure 5. Extinction coefficient k of four DuPont 157 nm immersion fluids at 32° C measurements were also made using the Woollam VUV-VASE® ellipsometer.

Table 2. Comparison of the extinction coefficients determined from minimum deviation prism measurements and those determined from relative transmission based absorbance measurements for three fluid thicknesses.

IF #		Rel. Trans. Abs./cm @ 157nm	Rel. Trans. Extinction Coeff @ 157nm	Min. Dev. Prism Extinction Coeff @ 157nm
IF24		1.33	3.84 x 10^{-6}	5.68 x 10^{-6}
IF26		1.10	3.17 x 10^{-6}	4.49 x 10^{-6}
IF48		1.00	2.89 x 10^{-6}	7.5 x 10^{-6}
IF53		NA (0.8)	NA (2.31 x 10^{-6})	NA (1.7 x 10^{-6})

CONCLUSIONS

Immersion fluids for 157 nm and 193 nm immersion lithography have been measured over the spectral range from 156 nm to 1700 nm in a nitrogen purged environment. The refractive index n and k of several candidate fluids have been measured using the prism minimum deviation technique implemented on a commercial Variable Angle Spectroscopic Ellipsometer (VASE®) system. For measurement the liquids were contained in a triangular prism cell made with fused silica windows. The refractive index of high-purity water at 21.5° C measured over the spectral range

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ACKNOWLEDGEMENTS

The authors would like to acknowledge the assistance of Sheng Peng, Weiming Qiu and Robert Wheland of DuPont Co. Central Research. This work was partially supported by International Sematech.

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