Immersion fluids for lithography: refractive index measurement using prism minimum deviation techniques

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ABSTRACT

As immersion lithography continues to develop at a rapid pace it will be necessary to determine the refractive index *n* and *k* of immersion fluids since the fluid becomes an important element of the optical system. The refractive index of several candidate immersion fluids for 193nm and 157nm immersion lithography is demonstrated using the prism minimum deviation technique. Measurements have been implemented on a commercially available variable-angle spectroscopic-ellipsometer system capable of operation into the vacuum ultraviolet. Results compare very well to high-accuracy reference measurements performed at NIST.

1. Introduction

Immersion lithography is rapidly emerging as a technique for extending optical lithography in semiconductor manufacturing several years by enabling device features to be printed with ever finer resolution [1,2]. In immersion lithography a fluid is placed between the final lens element of the exposure tool and the wafer to be exposed. The technique is similar to immersion microscopy, which has been used for over 150 years, but applying immersion techniques to microlithography has only been pursued in the last few years [1].

Shorter effective wavelength

In "dry" lithography tools the gap between the lens and the wafer is air having a refractive index n=1. Filling this gap with a fluid of refractive index greater than unity results in a shortening of the exposure wavelength by a factor of n according to:

$$\lambda_{\text{eff}} = \frac{\lambda_0}{n} \qquad (1)$$

where the wavelength in air or vacuum λ_0 is shortened to an effective exposure wavelength λ_{eff} in a fluid with refractive index n greater than unity.

193nm immersion

Immersion techniques are currently being implemented on 193nm lithography production tools by several manufacturers. Ultrapure water is currently being used as the immersion fluid in these 193nm exposure tools. Using water with a refractive index $n_{(193\text{ nm})}$=1.4366 in eqn (1) the 193nm exposure wavelength λ_0 can be reduced to λ_{eff} of 134 nm. This 30% reduction in exposure wavelength is achieved by changing the surrounding medium from air to water. This reduction in exposure wavelength through liquid immersion shows promise to extend the useful lifetime of 193nm lithography several years by printing smaller linewidth features than previously thought possible.

The 134nm effective wavelength is also attractive since it is already shorter than the 157nm exposure wavelength under consideration to succeed 193-nm lithography in the future. At the very least, successful implementation of 193-nm immersion techniques in production environments promises continued development time for 157nm and next-generation lithography (NGL) techniques such as extreme ultraviolet (EUV) lithography where much research and development still needs to be done.

157nm immersion, too

The same immersion techniques developed for use at 193nm can be applied equally well to 157nm lithography. However, different fluid chemistries are required for use at 157nm since the water-based fluids used for 193nm immersion quickly become opaque at wavelengths below 190nm. Several fluorinated liquids are being developed that are transparent at 157nm [2,3,7]. These current 157nm immersion fluids have lower refractive indices than 193nm fluids due to their strongly bonded fluorine-based chemistry. Continued research is ongoing into finding suitable 157nm immersion fluids with higher refractive index and lower absorbance.

193nm versus 157nm immersion: the importance of fluid index

Table 1 shows the impact of fluid refractive index on the effective exposure wavelength λ_{eff}. Both 193nm and 157nm exposure wavelengths are considered. Using different values for the refractive index n in eqn (1) it is clear that higher refractive indices result in shorter effective exposure wavelengths. Thus it is desirable to develop immersion fluids with as high a refractive index as possible. Currently, water is used for 193nm immersion, but water may be only the beginning for 193nm immersion lithography. Work is currently underway to find other fluids with higher refractive index for use in 193-nm immersion, promising to shorten λ_{eff} below the 134 nm obtained using water immersion. Table 1 shows that an immersion fluid with n=1.6 would provide a λ_{eff}=121 nm at an exposure wavelength of 193nm. Such a high-index fluid could extend the lifetime of 193nm lithography even further simply by substituting a different immersion fluid with higher refractive index.

TABLE 1: EFFECT OF FLUID REFRACTIVE INDEX ON λ_{eff}. BOTH 193-NM AND 157-NM EXPOSURE WAVELENGTHS ARE CONSIDERED. HIGHER REFRACTIVE INDEX FLUIDS GIVE A SHORTER EFFECTIVE EXPOSURE WAVELENGTH AND ALLOW PRINTING OF FINER FEATURES ON A WAFER.

Exposure wavelength, λ_0	**Fluid refractive index, *n***	**Candidate fluid**	**Effective wavelength, λ_0**
193 nm	1.4366	Water	134.6
193 nm	1.500	?	128.9
193 nm	1.600	?	120.9
157 nm	1.310	IF24	120.3
157 nm	1.326	IF48	118.9
157 nm	1.329	IF26	118.6
157 nm	1.362	IF43	115.7
157 nm	1.440	?	109.4

Table 1 also shows the advantages of 157-nm immersion lithography. Using an appropriate high-index fluid it would be possible to print even smaller features than with 193-nm immersion. Thus 157-nm immersion lithography will remain attractive to industry if suitable immersion fluids can be found with high enough refractive index to make 157-nm implementation worthwhile by printing features much smaller than those printable with 193-nm immersion. This would again extend the lifetime of optical lithography in semiconductor manufacturing.

The importance of *k*

The refractive index of any material is given by two numbers *n* and k, where *n* is the familiar refractive index and *k* is the lesser-known extinction coefficient. The values of both *n* and *k* vary with wavelength and also with temperature. Thus any given material will have different values for *n* and *k* at 193 nm and 157 nm. Both *n* and *k* are important to consider for immersion-lithography applications. The value of *n* determines the effective exposure wavelength through eqn (1) and is thus directly related to the ultimate resolution of the printed feature sizes. The index *n* also appears in the calculation of the numerical aperture of the exposure tool. The extinction coefficient *k* is a measure of the absorptive strength of a material. A lower *k* value indicates greater transparency, which results in shorter wafer exposure times in the exposure tool. Thus the *k* value of the immersion fluid is directly related to wafer throughput in a production environment. Lower *k* values will also result in less heating of the immersion fluid through absorption of light, which can lead to undesired thermally induced changes in the fluid refractive index.

Immersion fluid research

An "ideal" immersion fluid would exhibit an *n* value as high as possible at the exposure wavelength to enable printing the smallest possible features but with *k* as low as possible to minimize fluid heating and maximize wafer throughput. However, an "optimized" immersion fluid must also be chemically compatible with photoresists and may need to account for additional considerations such as matching the fluid index to that of the exposure tool lens material where the light beam emerges and also to the index of the resist layer into which the light beam must enter on the wafer. Many fluid chemistries will need to be investigated, so much work remains ahead to engineer optimal immersion fluids.

As research continues to find suitable immersion fluids, methods to easily screen candidate fluids for their optical properties *n* and *k* will be required. The prism minimum deviation technique is presented in this work. Measurement of fluid refractive index is expected to be a very active research area for the next several years as immersion techniques develop and find their way into production.

2. Experiment

The prism minimum deviation method

The prism minimum deviation method is commonly used to determine the refractive index of solid materials over a wide spectral range. Use of minimum deviation techniques for index measurements in the vacuum ultraviolet was pioneered by Burnett and Kaplan at NIST [4,5]. They have successfully adapted the technique for accurate measurement of water for use in 193-nm immersion [6] as well as fluorinated liquids for 157-nm immersion [7].

Figure 1 shows the geometry of a prism minimum deviation experiment for measurement of liquid samples. A hollow prism cell is used to contain the liquid. Window refraction effects cancel out in the symmetric cell so the index of the fluid is directly determined from measurement of the refracted beam transmitted through the cell. The refractive index of the material under study $n_{\text{fluid}}(\lambda)$ is given by:

$$n_{\text{fluid}}(\lambda) = \frac{\sin\left[\dfrac{A+\delta(\lambda)}{2}\right]}{\sin\left[\dfrac{A}{2}\right]}\, n_{\text{gas}}(\lambda) \qquad (2)$$

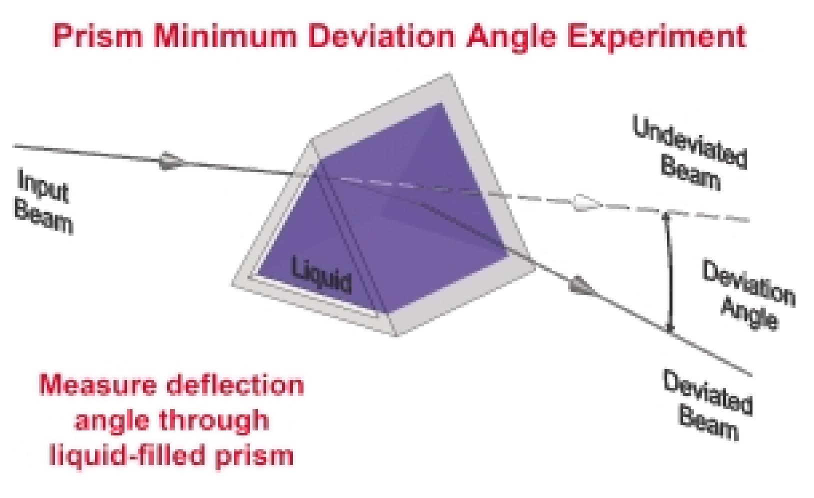

Figure 1. Geometry of prism minimum deviation measurements. Fluid is placed in a hollow prism and the deviation angle of the refracted beam is measured. The fluid refractive index is determined directly from the measured deviation angle.

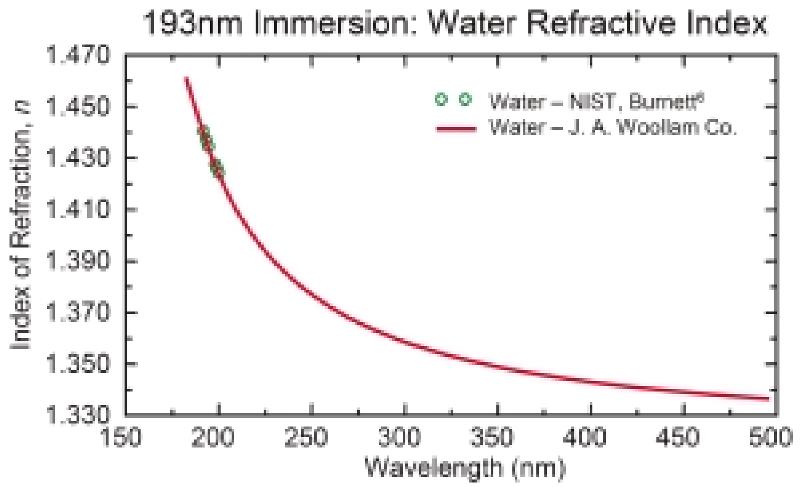

Figure 2. Refractive index of water at 21.5°C over the spectral range 185 to 500 nm. Water is the preferred fluid for use in 193-nm immersion lithography but is opaque below 185 nm. NIST reference values from Burnett are also shown with excellent agreement.

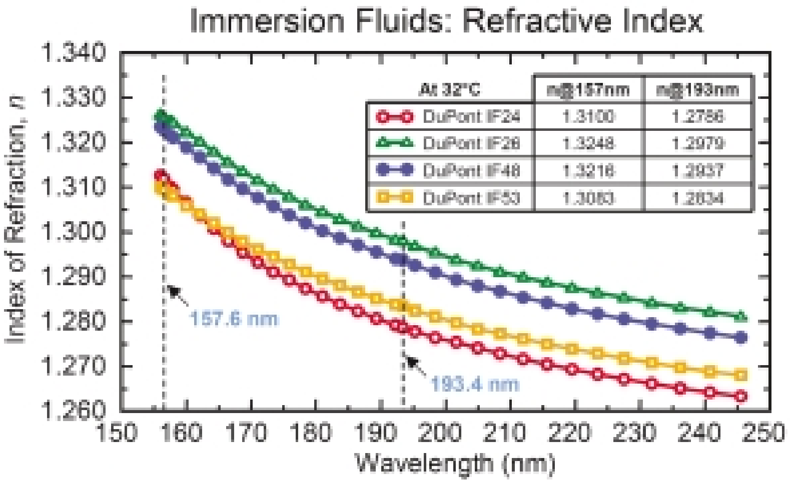

Figure 3. Refractive index of four DuPont 157 nm immersion fluids measured at 32°C. Measurements were made in a nitrogen-purged optical system to allow operation at wavelengths below 190 nm. Results at 157 nm and 193 nm are shown in the inset table.

where A is the prism apex angle, $\delta(\lambda)$ is the measured deviation angle, and $n_{gas}(\lambda)$ is the index of the surrounding ambient. With the apex angle and gas ambient constant, the refractive index is directly determined from the measured deviation angle $\delta(\lambda)$. The fluid index $n_{fluid}(\lambda)$ is determined by sweeping the angle to find the minimum deviation angle $\delta(\lambda)$ where light travels symmetrically through the prism. Once the minimum deviation angle is found the extinction coefficient $k_{fluid}(\lambda)$ can be determined by measuring the transmitted light intensity through the liquid for two or more cell positions with different path lengths.

Adapting prism measurements to ellipsometers

The continuously variable angle capability of research ellipsometers makes it possible to implement the prism minimum deviation technique on commercial ellipsometer instruments. When implemented on spectroscopic ellipsometers measurement at specific wavelengths of interest such as 193nm and 157nm can be performed, or the wavelength can be continuously varied allowing measurement of index over a wide spectral range. Continuous nitrogen purging allows measurements into the vacuum ultraviolet (VUV) spectral range below 190nm.

In this work the prism minimum deviation technique has been implemented on a J.A. Woollam Co. VUV-VASE® spectroscopic ellipsometer system capable of measurement over the spectral range from 140 to 1700nm. A liquid-filled prism cell is mounted on the sample stage to allow for fluid index measurements. Using a single instrument it is possible to measure both n and k of liquids over a wide spectral range provided the fluids are (semi)transparent at the wavelengths being measured. The experimental procedure is straightforward as no model fits are required as in conventional ellipsometry. The technique can be used to screen candidate immersion fluids for their optical properties n and k over the full spectral range of the instrument.

3. Results

193nm results for water

The refractive index of high-purity water was measured using the minimum deviation technique. The spectral dependence of the refractive index over the spectral range 185 to 500 nm is plotted in Figure 2. The solid line shows results measured on a J.A. Woollam Co. VUV-VASE® ellipsometer with a liquid prism cell. Results measured by Burnett and Kaplan at NIST [6] near 193 nm are shown as circles for comparison. Excellent agreement was obtained with the NIST values.

It was not possible to measure the water index below 185nm in this work because water absorbs strongly below 190 nm and is fully opaque at 185 nm and below. Thus water is suitable as an immersion fluid for 193-nm lithography, but not for 157-nm immersion where different chemistries with higher transparency are required.

157nm results on fluorinated liquids

Figure 3 shows the refractive index versus wavelength of four fluorinated liquids from DuPont plotted to 156 nm. At 157 nm the indices are in the range of 1.308 to 1.325. Figure 4 shows the extinction coefficient k of these same fluids. These measurements were performed at a temperature of 32°C. Work is currently underway to raise the refractive index n of 157-nm immersion fluids while simultaneously maximizing fluid transparency by lowering the value of k. Results for one such fluid is shown in Figure 5. It is possible to measure below 156 nm on (semi)transparent fluids by constructing the prism cell windows of a suitable material such as calcium fluoride or high-purity fused silica.

4. Conclusions

The useful lifetime of immersion lithography will be largely determined by the refractive index of the immersion fluids used. 193-nm immersion lithography is currently being implemented and should be useful for the next several years. 157-nm immersion lithography shows promise to print even finer features and further extend the lifetime of optical lithography provided suitable immersion fluids can be found. Measurements of both *n* and *k* using the prism minimum deviation technique have been implemented on a commercial spectroscopic ellipsometer with variable-angle capability. Agreement with highly accurate NIST measurements was found to be good for both 157-nm and 193-nm immersion fluids. Research into immersion fluids for 193- and 157-nm lithography is ongoing and expected to continue for several years.

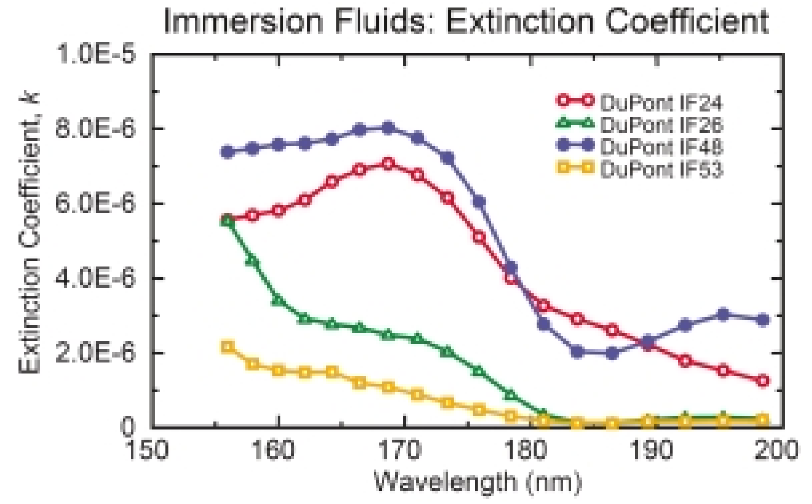

Figure 4. Extinction coefficient *k* for DuPont 157 nm immersion fluids shown in Figure 3. Lower extinction coefficients indicate higher transparency, which is important when considering wafer throughput in production environments. Higher transparency also results in less heating of the fluid through absorption of light.

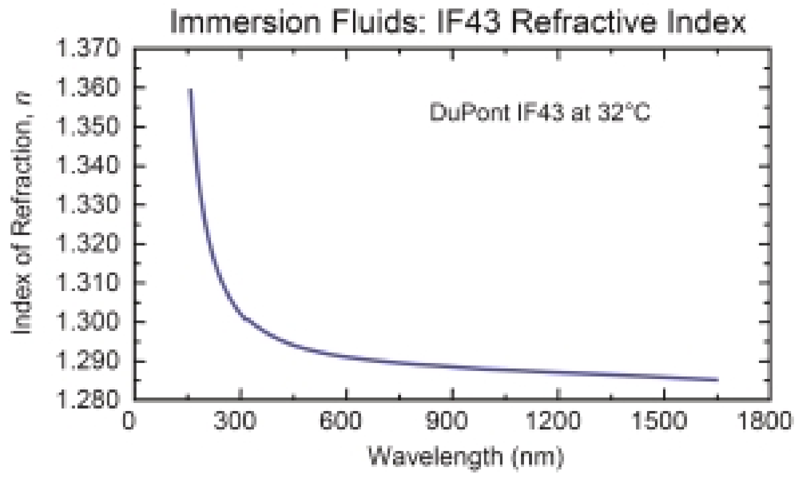

Figure 5. Refractive index of recent DuPont 157-nm immersion fluid at 32°C. Results are shown to 1,700 nm. For this fluid *n*=1.36 at 157 nm. A comparison with Figure 3 shows current research is yielding transparent fluids with higher index for 157-nm immersion work.

REFERENCES

[1] M. Switkes, M. Rothschild, R.R. Kunz, S.Y Baek, D. Cole and M Yeung, “Immersion Lithography: Beyond the 65 nm Node,” Microlithography World, May 2003, 4–20.

[2] M. Switkes, M. Rothschild, “Immersion Lithography at 157 nm,” J. Vac. Sci. Technol. B 19(6), Nov/Dec 2001, 2353–2356.

[3] R.R. Kunz et al., “Transparent Fluids for 157 nm Immersion Lithography,” Journal of Microlithography, Microfabrication, and Microsystems, 3, 1 (2004), 1–11.

[4] Rajeev Gupta, John H. Burnett, Ulf Griesmann and Matthew Walhout, “Absolute Refractive Indices and Thermal Coefficients of Fused Silica and Calcium Fluoride Near 193 nm,” Applied Optics, Vol. 37, No. 25, Sept. 1998, 5964–5968.

[5] John H. Burnett, Rajeev Gupta and Ulf Griesmann, “Absolute Refractive Indices and Thermal Coefficients of CaF2, SrF, BaF2, and LiF Near 157 nm,” Applied Optics, Vol. 41, No. 13, May 2002, 2508–2513.

[6] John H. Burnett and Simon Kaplan, “Measurement of The Refractive Index and Thermo-Optic Coefficient of Water Near 193 nm,” Proc. SPIE, vol 5040, Optical Microlithography XVI (2003).

[7] Roger H. French et al., “Immersion Fluid Refractive Indices Using Prism Minimum Deviation Techniques, Proc. SPIE, Vol. 5377, Optical Microlithography XVII (2004).

ENQUIRIES

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