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Determination of the Temperature Coefficient of the Refractive Index of Liquids for Immersion Lithography

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ABSTRACT

The refractive indices of solids and liquids are of great importance in many areas of research. In order to find a preferable immersion fluid for integrated circuit(IC) production the refractive index and its variation with temperature at different wavelengths of distilled water and with other solutions such as 1.0 M magnesium chloride ($MgCl_2.2H_20$), 1.0 M sodium chloride (NaCl), 1.0 M sodium hydroxide (NaOH) and 1.0 M H_2SO_4 have been studied. A good immersion fluid should have a high refractive index and a lower temperature coefficient compared with water. $MgCl_2.2H_2O$ was found to be the best solution having the highest refractive index and the lowest temperature coefficient of refractive index at different wavelengths of 578.00 nm 546.07 nm, 435.84 nm and 404.57 nm.

1. INTRODUCTION

The refractive index and the temperature coefficient of refractive index of liquids is very important in optical lithography. This is because the limitation of printing smaller feature sizes could be overcome by advancing imaging system on the substrate using a liquid with high refractive index to the space in between the projection lens and the photoresist. Then the minimum feature size that is printed could be minimized.

1.1 Optical lithography process

A reduction projection system, which is commonly used in optical lithography process, is shown in Fig. 1. A light source (usually a laser in order to obtain a monochromatic beam of radiation) shines light first through an illuminator, which expands, homogenizes, and conditions the beam, and then through a photomask, which contains the pattern to be imaged onto the wafer. The wafer is coated with a photosensitive material, called the photoresist. A complex projection lens reduces the photomask pattern by a factor (usually four or five), and images it onto the photoresist.

The exposed portions of the photoresist are removed at the development step, leaving behind the desired pattern on the photoresist, which is then transferred to the underlying wafer through an etch process. The sequence of coating the wafer with photoresist, exposing it with ultraviolet light, developing it, and etching it is repeated many times to complete the integrated circuit [1].

The performance of the projection system is determined by the laws governing the propagation of electromagnetic waves. In lithography, there are two major key components: *The resolution*, or the ability of the system to distinguish between nearby features, and *the depth of focus*, which is a measure of the precision with which the surface of the wafer must be positioned.

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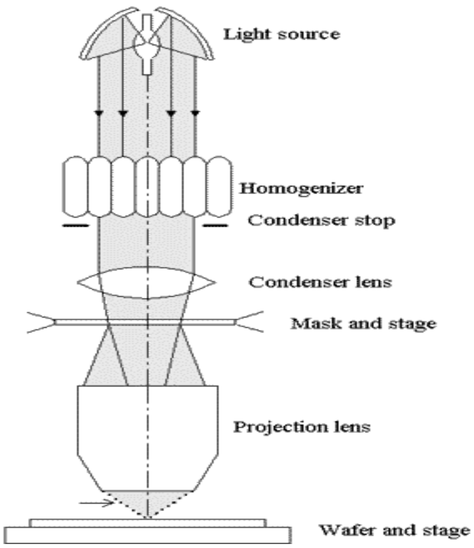

Fig. 1: Optical lithography system [2].

The minimum feature that can be printed with an optical lithography system is determined by the Rayleigh expression, given in equation (1)[3].

$$\mathbf{hp} = \frac{k_1 \lambda}{NA} \qquad (1)$$

Where hp is the 1:1 half pitch feature size, λ is the lithography wavelength, k_1 is a measure of lithography process capability, NA is the numerical aperture of the stepper's lens. NA is defined as given by equation (2)[3].

$$\mathbf{NA} = n_{IF} \sin \theta_{max} \qquad (2)$$

Where n_{IF} is the index of refraction of the immersion fluid at the lithographic wavelength and θ is the aperture angle, which is the angle, sustained by the ray of the largest spatial frequency permitted by the optical system.

The depth of focus is give by equation (3)[1].

$$\textbf{Depth of focus} = \frac{k_2 \lambda}{(NA)^2} \qquad (3)$$

Equation (1) indicates that improved resolution can be obtained by reducing the wave length λ of the laser and by increasing the NA of the imaging system. Continued improvements in optical lithography have enabled the printing of ever finer features, with the smallest size, or critical dimension, decreasing by about 30% every two years. On average, the number of transistors in an integrated circuit has doubled every eighteen months [4]. The physical limit to NA for exposure systems using air as a medium between the lens and the wafer is 1 [1].

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1.2 Liquid immersion lithography

Since the sine of any angle is always $\leq$ 1 and n = 1 for air, the physical limit for an air based system is clear, but if we have a medium with a higher index of refraction, the air should be substituted.

Liquid-immersion lithography achieves higher patterning resolutions without reducing the patterning wavelength λ as indicated in equation (1) but by increasing the NA beyond 1.0 through the use of immersion liquids. Equation (1) shows that, in addition to reducing λ and k_1, increasing the refractive index of the imaging medium results in higher resolution. Instead of air, we can employ a liquid with a refractive index n, which is greater than 1, and a resolution enhancement proportional to n is achieved without changing wavelength, lasers, photomasks, and other established components of the technology base.

Adding a liquid between the last optical element and the photoresist enables the coupling of rays that propagate at steep angles and that would otherwise be reflected through total internal reflection at the optics-air interface [1].

1.3 Temperature dispersion (dn/dT)

The change of refractive index of the immersion fluids as a function of temperature is an important parameter in the immersion lithography process. A low dn/dT, which has a value usually less than 2.50×10^{-2} /K is required for acceptable industrial application of immersion fluid [3]. Small changes in temperature are expected in the immersion liquid during the exposure to the beam. These variations should not cause changes in the refractive index of the fluid because if refractive index changes with temperature it would produce an uneven patterning image on the wafer.

2. EXPERIMENTAL PROCEDURE

A convenient formula for refractive index “n” can be obtained in the minimum deviation when a ray of light suffers deviation while passing through a prism. The deviation produced by the prism depends on the angle of incidence. If D_m denotes the angle of minimum deviation for a given prism of apex angle A, then the refractive index of the material of the prism n is given by equation (4).

$$\mathbf{n} = \frac{\sin\left[\frac{A+D_m}{2}\right]}{\sin\left[\frac{A}{2}\right]} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Equation (4) has been employed to calculate the refractive index of the liquids. Specially constructed hollow prism was used to measure the refractive index of liquids with the help of an optical spectrometer. The spectrometer was adjusted for parallel rays by using Schuster’s method.

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Apparatus was arranged according to figure 2. 100 ml of distilled water was put into a beaker and was heated up to 80^0C. Then the hollow prism was filled with the heated solution and was placed in the middle of the prism table. Then the prism was adjusted to its minimum deviation position by adjusting the prism table and by observing through the telescope. The prism table was locked at this position. The temperature probe of the multimeter was inserted in the liquid without disturbing the incoming light rays and without touching the surface of the glass walls.

The multimeter was turned on and switched to temperature mode and the cross hairs of the telescope was focused to the Na d-line and relevant spectrometer reading was recorded when the temperature was at 64^0C. Same procedure was repeated for the temperature intervals of 4^0C and relevant spectrometer readings were recorded until the temperature reached to 30^0C. Then the prism was removed from the table and the direct reading was also taken.

The sodium lamp was replaced with the mercury lamp. Another 100 ml of distilled water was heated up to 80^0C and the prism was filled with the hot solution. Then the prism was kept in the middle of the prism table and this time cross hairs of the telescope were focused to the minimum deviation position of the yellow line of the spectrum. The cross hairs were focused to the yellow line for temperature intervals of 4^0C. The relevant spectrometer readings were recorded. Same procedure was repeated for the green line.

1.0 M Magnesium chloride, 1.0 M Sodium chloride, 1.0 M Sodium hydroxide and 1.0 M sulfuric acid solutions were prepared. The same procedure was repeated for each of these solutions for the spectral lines yellow, green, blue and violet and the relevant spectrometer readings were recorded.

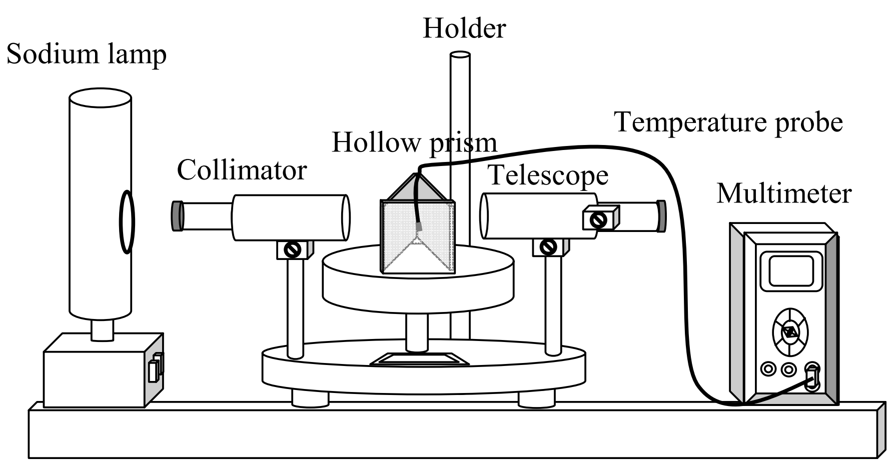

Fig. 2: Experimental arrangement of the apparatus.

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3. RESULTS AND DISCUSSION

The variation of the refractive indices with temperature of distilled water, 1.0 M magnesium chloride ($MgCl_2.2H_20$), 1.0 M sodium chloride (NaCl), 1.0 M sodium hydroxide (NaOH) and 1.0 M H_2SO_4 at different wavelengths are presented in figures 3, 4, 5 and 6, respectively. $MgCl_2.2H_2O$ solution gave the highest refractive index at 337.15 K and all the other liquids had refractive index lower than that value. By using Micocal origin 6.0 software the experimental data were subjected to linear curve fitting and the temperature coefficient of the refractive indices of each liquid at each wavelength are presented in the Table1.

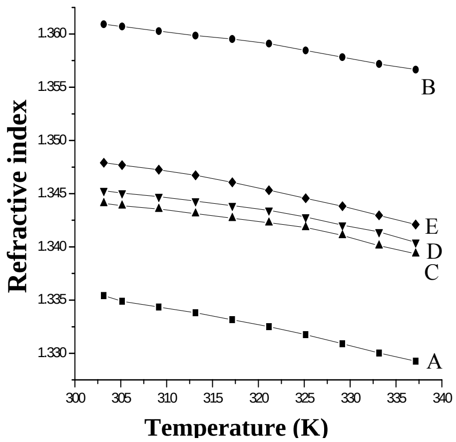

Fig. 3: The variation of refractive index versus temperature of A- distilled water, B - 1.0 M $MgCl_2.2H_20$, C - 1.0 M NaCl, D - 1.0 M NaOH and E - 1.0 M H_2SO_4 for yellow line (578.00 nm).

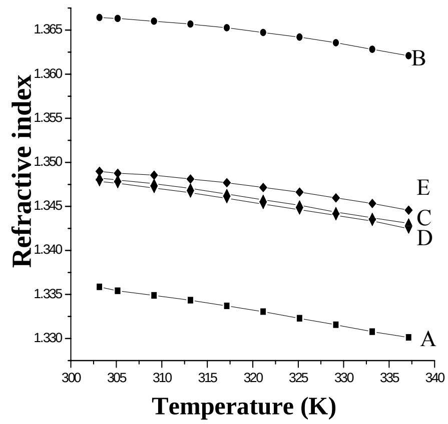

Fig. 4: The variation of refractive index versus temperature of A- distilled water, B - 1.0 M $MgCl_2.2H_20$, C - 1.0 M NaCl, D - 1.0 M NaOH and E - 1.0 M H_2SO_4 for green line (546.07 nm).

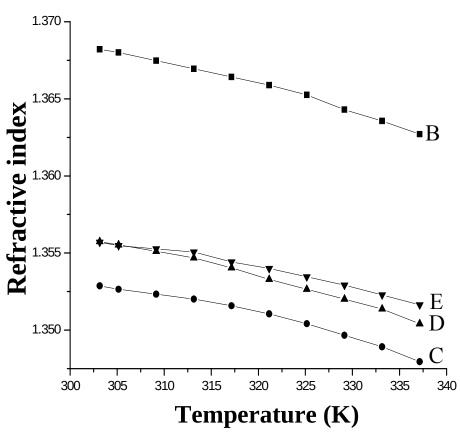

Fig. 5: The variation of refractive index versus temperature of B - 1.0 M $MgCl_2.2H_20$, C - 1.0 M NaCl, D - 1.0 M NaOH and E - 1.0 M H_2SO_4 for blue line (435.84 nm).

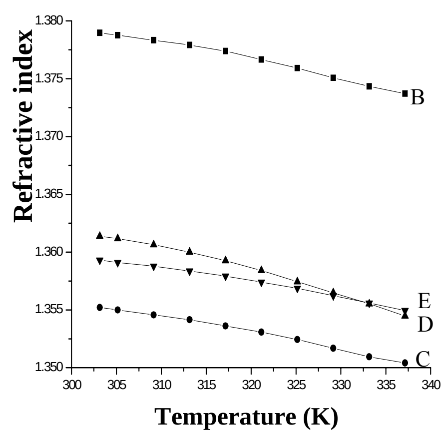

Fig. 6: The variation of refractive index versus temperature of B - 1.0 M $MgCl_2.2H_20$, C - 1.0 M NaCl, D - 1.0 M NaOH and E - 1.0 M H_2SO_4 for violet line (404.57 nm).

According to the Table 1, water has the highest value of dn/dT compared to the other four liquids. Thus it is not a suitable solution for immersion lithography. NaCl, H_2SO_4 and $MgCl_2.2H_20$ have very low dn/dT than distilled water and NaOH. According to Figs. 3, 4, 5 and 6 it is obvious that 1.0 M $MgCl_2.2H_20$ has a higher refractive index than others at every wave length.

Table 1: Temperature coefficient of refractive index of liquids.

	Temperature coefficient of refractive index ($\times 10^{-4}$ K^{-1})				
	Na D Line (589.30 nm)	**Yellow (578.00 nm)**	**Green (546.07 nm)**	**Blue (435.84 nm)**	**Violet (404.57 nm)**
Distilled water	-1.96969 ± 0.12100	-1.77127 ± 0.04849	-1.67582 ± 0.03227	-	-
$MgCl_2.2H_20$	-	-1.24399 ± 0.04801	-1.26266 ± 0.07353	-1.59636 ± 0.06523	-1.58194 ± 0.06625
NaCl	-	-1.33663 ± 0.08584	-1.54273 ± 0.03797	-1.39361 ± 0.09050	-1.43145 ± 0.5140
NaOH	-	-1.36628 ± 0.07834	-1.56352 ± 0.03371	-1.55278 ± 0.05526	-2.04616 ± 0.08105
H_2SO_4	-	-1.7187 ± 0.06352	-1.27336 ± 0.06315	-1.18621 ± 0.06020	-1.2736 ± 0.04943

Predictions of refractive indices at very low wavelengths (95 nm) can also be done if more wave lengths of light would have been employed for the experiment.

Correlations could have been predicted if more wave lengths were used in the experiment. Predicting refractive index of the liquid at any wavelength could have been done by using these relations.

Air has an index of refraction n = 1, Putting n = 1 into the following equation and assuming $\sin\theta$ can reach 0.93, then the resolution limits for 404.565 nm immersion lithography are

$$hp = \frac{0.25 \times 404.56 \text{ nm}}{1 \times 0.93} = 108.75 \text{ nm}$$

Water has an index of refraction n ≅ 1.34414 at 303.15 K, Putting n = 1.34 into the following equation and assuming $\sin\theta$ can reach 0.93, then the resolution limits for 404.565 nm immersion lithography are

$$hp = \frac{0.25 \times 404.565 \text{ nm}}{1.34 \times 0.93} = 81.12 \text{ nm}$$

$MgCl_2.2H_20$ has an index of refraction $n \cong 1.37897$ at 303.15 K, Putting n = 1.37 into the following equation and assuming $\sin\theta$ can reach 0.93, then the resolution limits for 404.565 nm immersion lithography are

$$hp = \frac{0.25 \times 404.565\ \text{nm}}{1.37 \times 0.93} = 79.38\ \text{nm}$$

As for the above values it can be seen that introducing liquids with higher refractive index can lower the minimum feature size, which could eventually be printed on a circuit board. $MgCl_2.2H_20$ showed that the minimum feature size was at 404.57 nm.

4. CONCLUSION

It is always desirable for industrial applications to have a liquid with a higher refractive index usually greater than that of water, and the temperature coefficient of the liquid which should be less than 250 ppm/K. According to the results, almost all the liquids tested had lesser values for dn/dT than 250 ppm/K. But $MgCl_2.2H_20$ and H_2SO_4 had considerably high refractive index than water. Therefore they can be employed as preferable immersion fluids.

$MgCl_2.2H_20$ and H_2SO_4 can be employed as immersion fluids at 404.565 nm. $MgCl_2.2H_20$ solution provided the minimum feature size, which could be printed as 404.57 nm.

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Refractive index