Phosphoric Acid as a High-Index Immersion Fluid

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Abstract—**A study has been performed to determine the viability of phosphoric acid as a high-index fluid for immersion lithography. The ability to image in the immersion fluid, and the compatibility of the fluid with photoresist were examined. Samples were soaked in the fluid before and after exposure in water to demonstrate no significant damage to the imaging capability of the resist. The refractive index of photoresist samples soaked in various immersion fluids was measured with a variable angle spectroscopic ellipsometer (VASE), and results did not show a significant variation from photoresist that was not soaked. Sixty-eight nanometer lines were imaged through phosphoric acid in 193nm photoresist without a topcoat layer.**

Index Terms—**Immersion lithography, interferometry, high-index fluid**

I. Introduction

OPTICAL lithography has played a critical role in the advancement of the semiconductor industry and is expected to take industry to at least the 65 nm node and possibly beyond [1]. Throughout the past two decades, lithography pushed the physical limits of optical lithography through three main trends: (1) reduction in exposure wavelength; (2) increase in numerical aperture (NA) of projection systems; and (3) implementation of resolution enhancement techniques such as phase shifting masks and off axis illumination leading to a reduction in the k_1 factor [2].

Resolution of diffraction-limited optical lithography is generally defined by the Rayleigh criteria

$$R = k_1 \lambda / NA, \quad (1)$$

where R is the minimum dimension, or pitch, that can be printed, k_1 is the process dependent resolution factor, λ is the exposure wavelength, and NA is the numerical aperture of the projection lens. The resolution factor, k_1, is typically between 0.6 and 0.8, and is dependent on the process used for exposure. The NA value is dependent on the optical system and is defined as $n_i \sin\Theta_0$, where Θ_0 is the angle of acceptance of the lens, and n_i is the refractive index of the medium surrounding the lens. For typical optical lithography, the medium surrounding the lens is air. Therefore, the maximum NA achievable is 1.00, since the refractive index of air is 1.00 [2].

Historically, significant improvements in resolution have been the result of shrinking exposure wavelength. Another method to achieve smaller resolutions is to increase the refractive index between the lens and the photosensitive substrate. One way this has been accomplished is to place a liquid with a high refractive index between the projection lens and the photoresist during exposure. This technique is referred to as immersion lithography. The resulting resolution enhancements can be quantified by an increase in NA of the system. However, NA is not the only factor affected. The system can also be modeled by scaling the exposure wavelength to the effective wavelength in the given medium. This wavelength, λ_{eff}, is equivalent to λ_0/n_i, where λ_0 is the wavelength in vacuum, and n_i is the refractive index of the immersion medium. As the fluid refractive index increases, the minimum pitch that can be imaged will decrease, as defined by Equation 2 [3].

$$R = \frac{k_1 \lambda_{eff}}{\sin \Theta_0} \quad (2)$$

Through the increase in index between the projection lens and the photoresist, the depth of focus (DOF) also improves, as illustrated in Figure 1.

There are many aspects to consider when imaging with an immersion system. The immersion fluid of choice must be compatible with the photoresist to be used, and must have a high refractive index at the wavelength of interest In addition, polarization, bubbles, and the absorption spectra of the immersion fluid can affect immersion imaging [3].

Water is a common immersion fluid because of its high refractive index (1.44 at 193nm), and compatibility with lithography systems and resist. However, other high-index fluid options are being studied. A viable immersion fluid for 193 nm lithography needs an absorption peak below 193 nm, and a high refractive index at that wavelength. This project explores the photoresist compatibility and imaging capability of phosphoric acid (H_3PO_4) in water as an immersion fluid. The absorption peak of the hydrogen phosphate in solution is at a

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wavelength of 170 nm, and the refractive index of the 85% (by weight) phosphoric acid in water is 1.54 at 193 nm.
Thus, phosphoric acid is a viable candidate for high-index immersion lithography at 193 nm.

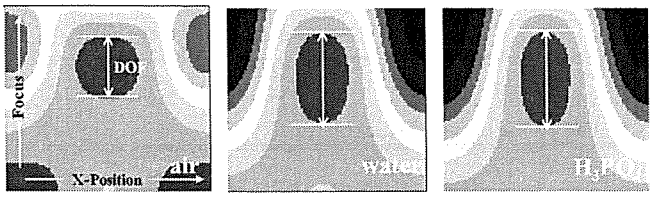

Fig. 1. Image intensity in resist shows increased depth of focus for increased refractive index of the immersion medium. Left: exposed in air (n=1.0003). Center: exposed in water (n=1.437). Right: exposed in 85% phosphoric acid solution (n=1.54).

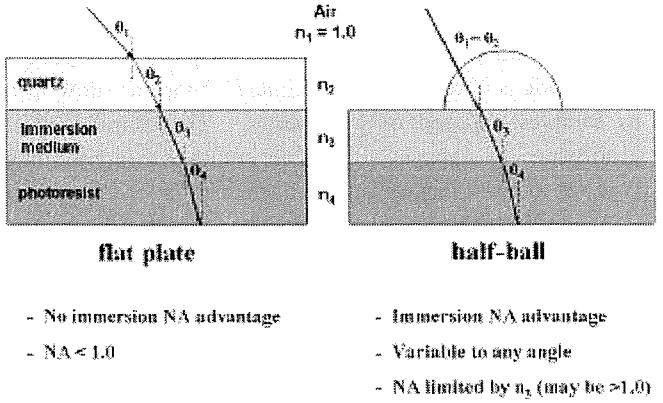

Fig. 2. Left: Immersion lithography using a flat plate. Right: Immersion lithography using a half ball.

II. Experimentation and Results

A simple and effective way to implement immersion lithography is with an interferometric system (Figure 4). Interferometric lithography offers high contrast over a large range of special frequencies, and is well suited for the study of alternate immersion fluids [4].

Interferometric lithography utilizes two mutually coherent beams of wavelength ? that are incident on a photosensitive substrate. Their wave vectors are coplanar and each make an angle ? with respect to the normal to the substrate, as shown in Fig. 3. Interference of the two plane waves produces a sinusoidal intensity pattern, with period ? given by Equation 3 [4].

$$\Lambda = \frac{\lambda_0}{2 \sin \Theta} \qquad (3)$$

As ? approaches 90°, ? approaches the limiting value of ?/2, which corresponds to the highest spatial frequency that is theoretically achievable with freely propagating light beams of a given wavelength in air. For light propagating through an optically dense medium, a finer grating is formed with a period

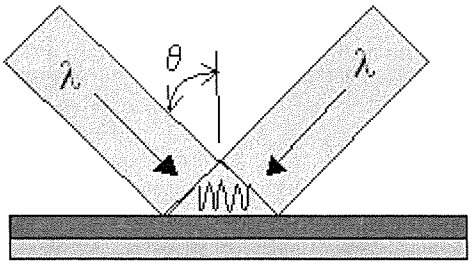

Fig. 3. Two mutually coherent beams of wavelength ? interfere at the surface of a photosensitive substrate to form a sinusoidal standing wave pattern.

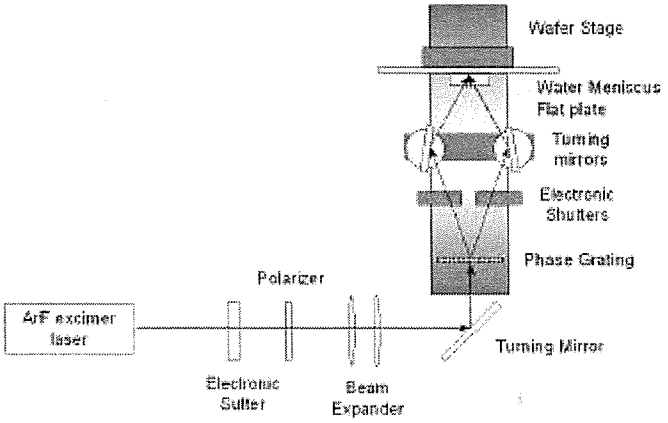

Fig. 4. 193 nm Immersion Interferometric Lithography Micro-exposure Tool

$$\Lambda = \frac{\lambda_0}{2 n_i \sin \Theta}. \qquad (4)$$

The high index fluid is placed between a quartz piece and the substrate in order implement immersion lithography on the interferometric system. However, for an immersion interference system, the NA advantage is only possible if the two interfering beams enter normal to the quartz surface, as shown in Figure 2. Thus, a "half-ball" or a prism must be used to realize the advantages of immersion imaging. In a flat plate setup, shown in Figure 2, the immersion advantages cancel out, and there is no image improvement observed. To demonstrate the ability to image through the fluid, this project utilizes a flat plate. Thus, the pitch imaged in the resist will be defined by the limits of the interference system without an advantage due to the high refractive index of the fluid.

Five samples were exposed in Ultra Pure Water under various conditions using an ArF 193nm excimer laser coupled with the interferometric system. The five conditions are as follows:

1) Soaked 60 seconds in H_3PO_4 (47% solution) and rinsed 30 seconds in H_2O before exposure
2) Soaked 90 seconds in H_2O before exposure
3) Soaked 60 seconds in H_3PO_4 (47% solution) and rinsed 30 seconds in H_2O after exposure
4) Soaked 90 seconds in H_2O after exposure
5) Not soaked before or after exposure.

Images collected from these samples, shown in Figure 6, demonstrate imaging in photoresist soaked in 47% by weight

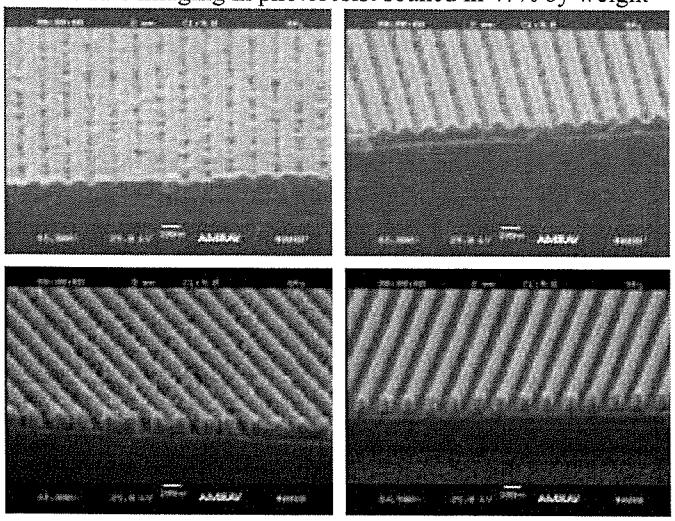

Figure 5 Samples exposed in Ultra Pure Water. Top-left – phosphoric acid presoak, Top-right – phosphoric acid postsoak, Bottom-left – water presoak, Bottom-right – water postsoak.

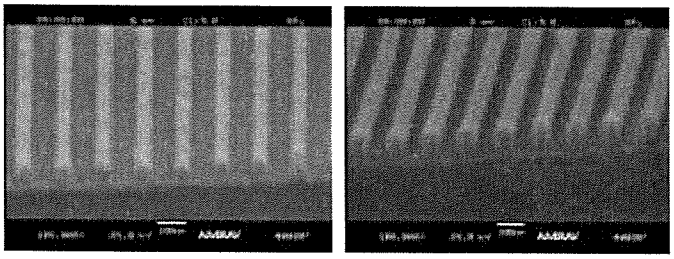

Figure 6 Samples exposed in Phosphoric Acid (H_3PO_4). Left: 47% H_3PO_4 solution. Right: 85% H_3PO_4 solution.

phosphoric acid in water. Resist scumming is observed on samples soaked in the acid. However, this may be the result of an insufficient exposure dose.

A second set of samples was then exposed in the phosphoric acid solution instead of water. These samples were not soaked before or after exposure. The first of the samples was exposed in the 47% phosphoric acid solution, and the second was exposed in 85% solution. Sixty-eight nanometer lines were imaged in each case in resist without a top-coat layer.

Finally, a variable angle spectroscopic ellipsometer (VASE) was used to explore effects of the fluid on the photoresist. The refractive indexes of the following three resist samples were measured:

1) Unexposed resist soaked in water for 90 seconds
2) Unexposed resist soaked in phosphoric acid (85%) for 60 seconds and rinsed in water for 30 seconds
3) Unexposed resist (not soaked)

The results were analyzed using Wollen VASE (WVASE) software to fit the collected data using a Lorentz model. Table I shows the resist refractive indexes measured. No significant difference is observed between the samples soaked in water and in the phosphoric acid solution.

TABLE I
REFRACTIVE INDEX MEASUREMENTS

Condition	Resist Refractive Index
No soak	1.70
Water soak	1.71
Phosphoric acid (85%) soak	1.71

III. DISCUSSION AND CONCLUSIONS

Phosphoric acid did not destroy the photoresist used in the experiment. The samples soaked in acid, illustrate some scumming compared to the water soaked samples. However, this is a result of the exposure conditions rather than a damaged photoresist. Samples soaked or exposed in phosphoric acid required approximately twice the dose to clear as samples exposed only to water. This implies that the absorbance of phosphoric acid in solution is approximately twice as much as that of water at a wavelength of 193nm.

The samples exposed in phosphoric acid illustrated the ability to image through both 47% and 85% phosphoric acid solution using an ArF excimer laser. Sixty-eight nanometer lines and spaces were imaged in the Shipley resist with no signs of T-topping.

The ellipsometer data collected shows negligible variation between the resist samples soaked in the immersion fluids. As shown in Table I, the refractive index of the samples soaked in the immersion fluid was slightly higher than the sample not soaked in fluid. This indicates a possible change in the properties at the surface of the photoresist. However, the full effects of the fluid on the resist cannot be determined through this measurement alone.

Phosphoric acid is a viable high-index fluid candidate for immersion lithography. The acid has not demonstrated significant damage to the resist properties, and imaging through the fluid has been achieved. Further work must be completed to determine the full effect of the immersion fluid on photoresist.

APPENDIX

A. Sample Preparation

To carry out the experiment, five four-inch wafers were coated with a Shipley bottom anti-reflective coating or BARC, and Shipley 193nm photoresist using the process below.

1) Spin on Shipley AR-40 BARC
   a. Spin speed = 2300 RPM
   b. Post Apply Bake (PAB) = 215°C, 60 sec.
2) Spin on Shipley XP1020 193nm photoresist
   a. Spin speed = 3500 RPM

b. PAB = 120°C, 90 sec.

Samples were then exposed according to the conditions described. Post exposure bake was set at 120° C for 60 seconds. Then, samples were developed in CD-26 developer for 60 seconds, rinsed 30 seconds in water, and blown dry with a nitrogen gun.

In preparation for SEM pictures, each sample was cleaved and sputtered with gold. Images were collected on an Amray SEM.

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Karen R. Wolf, originally from Binghamton, NY, received a B.S. degree in Microelectronic Engineering from the Rochester Institute of Technology in 2004. She obtained co-op work experience at Micron Technology in Manassas, VA.