The Interaction of Ultra-Pure Water and Photoresist in 193nm Immersion Lithography

James H. Park

Abstract— **The proposed paper investigates the effects of ultra-pure water on DUV photoresist used in 193 nm immersion lithography. Microlithography is the key technology that is pacing Moore's Law. With critical transistor features reaching the 45nm device node, the development for new techniques in optical lithography are well underway. Large investments have been made into the Next Generation Lithography (NGL) technology development such as VUV (vacuum ultraviolet) and EUV (extreme ultraviolet) projection lithography. However, an extension of optical imaging at 193 nm deep ultraviolet (DUV) to immersion lithography at the same wavelength offers considerable potential for it to be used as a next step in production, postponing the introduction of EUVL.**

Index Terms—**193nm Immersion Lithography, EXITECH, Microstepper, Photoresist, SEM (Scanning Electron Microscope) and Ultra-pure water**

I. Introduction

Immersion lithography technology involves the use of an immersion fluid between the lens and the wafer to enhance the patterned image in the photoresist. This phenomenon is based on the discovery by Ernst Abbé in the 1870's, who enhanced his microscope by using oils that matched the index of refraction of the glass. The matching index of refraction prevents reflective effects at the interfaces of the lens and the sample. By using ultra-pure water between the objective lens and the wafer, the resolution of the features could be theoretically enhanced by 43% due to the difference of indices between water and air.

This project focuses on the study of interaction of water and 193 nm photoresist materials. Contact time of photoresist with ultra-pure water was varied in order to determine the impact water has on the imaging performance. Test exposures were carried out on the RIT's 193 nm 1.05NA projection immersion microstepper. Quantitative results such as sidewall angle, post-exposure delay sensitivity and image quality were compared. With these results, an optimum process for the immersion lithography at 193nm can be engineered here at RIT.

Manuscript received October 9, 2001. (Write the date on which you submitted your paper for review.) This work was supported in part by the U.S. Department of Commerce under Grant BS123456 (sponsor and financial support acknowledgment goes here). Paper titles should be written in uppercase and lowercase letters, not all uppercase. Avoid writing long formulas with subscripts in the title; short formulas that identify the elements are fine (e.g., "Nd–Fe–B"). Do not write "(Invited)" in the title. Full names of authors are preferred in the author field, but are not required. Put a space between authors' initials.

F. A. Author is with the National Institute of Standards and Technology, Boulder, CO 80305 USA (corresponding author to provide phone: 303-555-5555; fax: 303-555-5555; e-mail: author@ boulder.nist.gov).

S. B. Author, Jr., was with Rice University, Houston, TX 77005 USA. He is now with the Department of Physics, Colorado State University, Fort Collins, CO 80523 USA (e-mail: author@lamar. colostate.edu).

T. C. Author is with the Electrical Engineering Department, University of Colorado, Boulder, CO 80309 USA, on leave from the National Research Institute for Metals, Tsukuba, Japan (e-mail: author@nrim.go.jp).

II. Theory

A. Lithography

Moore's Law states that the number of transistors per square inch would double every year, however in actuality, the number of transistors has doubled about every 18 months [4]. Photolithography is a major component to the drive of IC manufacturing and is the main factor in improving the complexity and cost of IC's. The improvements are made through the ability of lithography to pattern smaller and yet smaller feature sizes. Since the mid-eighties, optical lithography was predicted to become obsolete within a few years. However, every time optical lithography approaches a limit, new and advanced techniques seem to prolong the life of the technology. Recently however, optical lithography has encountered several physical barriers, which have led to an immense investment in alternative techniques such as Scalpel (ebeam), EUV (extreme ultraviolet lithography [projection]) and a few others.

B. Resolution

Rayleigh equation governs the minimum feature that can be printed using an optical lithography system:

$$\mathbf{R = k_1 \lambda / NA},$$ where,

R = resolution
k_1 = resolution factor
λ = wavelength of exposing radiation
NA = numerical aperture of the system.

As the resolution of minimum features have shrunk, the wavelength of the exposing wavelength has also shrunk. A table below shows the gradual decrease of feature width (CD – critical dimension) as well as the decrease in wavelength used as a function of years.

C. *Wavelength Requirements*

Year	Linewidth (nm)	Wavelength (nm)
1986	1200	436 g-line mercury lamp
1988	800	436/365
1991	500	365 i-line mercury lamp
1994	350	365/248
1997	250	248 KrF excimer laser
1999	180	248
2001	130	248
2003	90	248/193
2005	65	193 ArF excimer laser
2007	45	193/157

Table 1:Minimum Linewidths in IC processing since 1986 [1]

Below 193nm wavelength is the 157 nm Fluorine (F_2) excimer laser which faces great challenges. (This is due to the fact that at this wavelength the optical exposure systems have to switch over to reflective optics due to high levels of absorption in the refractive lens. Mention other challenges)

Along with the shortening of wavelengths, improvements in lens design have led to the increase in NA (numerical aperture) of the exposure systems lens. The gradual increase of NA (max = 1.0 in air) values has given lithographers the ability to produce features of higher resolution.

The last factor in Reyleigh equation is the k_1 value. This value contains the variables in the photolithographic process such as resist quality, thermal bakes and resolution enhancement techniques, also known as RET, such as phase shift masks and off-axis illumination. The values of k_1 have been decreasing over the last twenty years. The practical lower limit for k_1 is thought to be ~0.25. Hence the trends to achieving smaller features or better resolution are as follows: decrease λ, increase NA and maximize k_1.

D. *Immersion (H_2O)*

Having introduced the art of microlithography and its gradual development in IC processing from the mid-eighties, companies are looking into a technology which is being considered the 'next generation lithography' [2]. *Immersion lithography*, which involves altering the medium at which exposure takes place, has lithographers grabbing the closest cup of water. Ernst Abbe first discovered in the 1870's that the maximum ray slope entering a lens, could be increased by a factor equal to the refractive index of the imaging media [2]. Abbe used oils between his microscope objective and the cover glass with refractive indices close to that of glass to increase the resolution of the images that were produced by the scope. The concept was simple yet revolutionary, by matching the refractive indexes of the mediums he prevented the interference effects on the image. The first application of this 'new technology' came in the field of medical research where Carl Zeiss and Abbe developed oil immersion systems through the used of oils that match the refractive index of glass (~1.5000).

Previous optical exposure systems had a physical limitation to NA (NA =1.0) due to the medium of air (n~1.0003) in between the lens and the wafer. Numerical aperture is determined by the acceptance angle of the lens and the index of refraction of the medium surrounding the lens [1]. By altering surrounding medium, hence the refractive index of the medium, a larger value of NA can be achieved. However, this will involve the 'new' medium having a refractive index greater than 1.0, have low absorption at 193nm, be compatible with the photoresist and lens material and most importantly have non-contaminating qualities. Another vital requirement is an objective lens that allows for larger ray angles and allows the angles to interface with the immersion fluid. The most frequently used for form of immersion lens is a hemispherical lens or a prism [2].

Surprisingly, ultra-pure water (H_2O) may be the magic solution to be used as the immersion fluid. Water has absorption values below 0.50 cm^{-1} @ 185nm and below 0.05 cm^{-1} at 193nm In other words, at 193nm wavelength the absorption is below 5% at working distances of up to 6mm [1]. The refractive index of water is 1.437 which will effectively decrease the wavelength to 134nm and also increase the NA of the imaging system to 1.437*NA. This enhancement will result in a potential 43% improvement, which is twice that of going from 248nm to 193nm, 193nm to 157nm or 157nm to 126nm exposure wavelengths without immersion technology [2]. As the NA nears ~1.44, resolution enhancement to **35nm** is theoretically plausible.

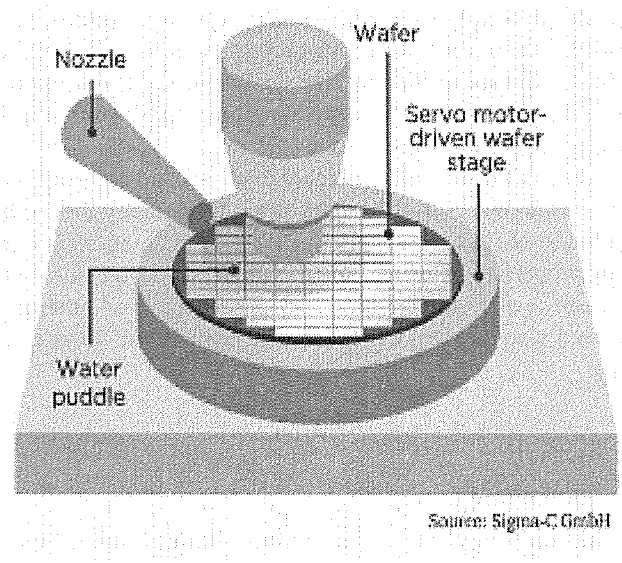

Figure 1: Immersion Lithography Exposure System [5]

E. Challenges

Below is a table comparing the challenges for lithography at UV/DUV/EUV optical wavelengths and the solutions of such challenges using immersion lithography at 193nm.

UV/DUV/EUV	IL @ 193nm
UV resists release great volumes of dissociated nitrogen upon exposure	193nm resist platforms release relatively low volumes of gas upon exposure
High index fluids tend to react with photoresist	Reaction of water with 193nm photoresist is minimal and can be reduced through modification
Standard immersion fluids are not transparent below 300nm	Water is transparent below $0.05cm^{-1}$ @ 193nm
Wafer handling processes of fluid wetting, cleaning and drying	Water is an existing component of wafer processing

Table 2: Challenges of UV/DUV/EUV lithography vs. IL @ 193nm

There are number of challenges yet to face with immersion lithography. Several prototypes have been developed to help measure the important parameters that must be taken into consideration. One of the fundamental issues is the compatibility of water with conventional lithography components. Also, in order to achieve high throughput, the stage must move from field to field quickly as possible and maintain a bubble free liquid between the lens and the wafer. There have been several approaches that have been developed to tackle this problem. The most probable to be used is a technique that involves a nozzle that will dispense a 'puddle' of water under the lens in between the wafer and the objective. Another issue will be maintaining the temperature of the system environment, which may affect the refractive index and hence the image resolution. The challenge will be to maintain the temperature when the stage is moving rapidly and a pulsed laser passes through the system [1].

Overall, there are still a number of issues and challenges that still need to be resolved in immersion lithography technology. The main challenges include the overall imaging capabilities, fluid properties of water (micro-bubbles) and the interaction between water and photoresist. The study of interaction between water and 193nm photoresist will be the focus of this paper.

III. EXPERIMENT

The objective of the project was to determine the interaction of water with photoresist in 193nm Immersion Lithography. In order to simulate the contact of water with the photoresist before exposure, coated wafers were soaked in ultra-pure water for different intervals. Intervals were: 1min, 2min, 4min, 8min, 16min, 32min and 64min. These times were chosen to accommodate a wide range of soak times from 1min to over an hour.

The film stack used in this experiment is as follows:

- BARC: Shipley AR40-800
  - 1230rpm, t=826Å
  - PAB: 215°C ~60sec
- Photoresist: Shipley XP 1020B
  - 1090rpm, t=1500Å
  - PAB: 120°C ~60sec
  - PEB: 120°C ~90sec
- Developer: CD-26

[All wafers were processed on the Brewer Science Stand-Alone Developer/Coater Equipment]

After the soak in water, the wafers were dried off and exposed on the EXITECH system. Using a binary mask at 0.7s, 100μm fields were exposed on the wafer. The mask consists of lines and spaces ranging from 80nm~300nm (80nm, 100nm, 120nm, 140nm, 160nm, 180nm, 200nm, 250nm and 300nm) with each set having 9 lines and spaces. All the wafers (8 intervals) were exposed with a FEM (Focus Exposure Matrix) of 21x17 with the focus varying from 5~7μm (inc. 0.1μm) and dose varying from $8\sim12mJ/cm^2$ (inc. $0.25mJ/cm^2$).

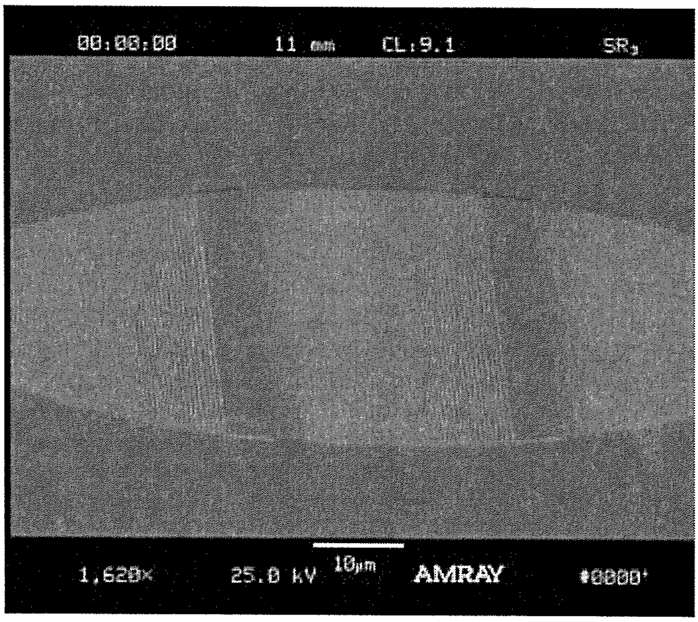

Figure 2: 100μm field exposed on the EXITECH tool

Using an optical microscope, the dies with the optimum focus and dose were recorded for further SEM work. Using the recorded values as a guideline, SEM work was done in order to obtain images of 80nm, 100nm and 120nm lines and spaces. The results were compared and contrasted to detect any trends that may occur due to the soak in water prior to exposure. Line Edge Roughness (LER), leaching effects, T-topping and any

signs of contamination were investigated.

The analysis of results was very qualitative in this experiment. The quality of lines and spaces of three different sizes at different soak times were studied. By detecting any kind of pattern due to the soaking will help identify any effects of the water on the immersion photoresist.

IV. Results and Analysis

SEM results were obtained using the AMRAY SEM at Rochester Institute of Technology. With considerations to the dose uniformity of the fields, the images were captured at the same exact locations for each die in order to achieve consistency in the results. Optically, the best focus range was, 5.7~6.1μm and the best dose range was, 8~10.5mJ/cm^2. Using this data, dies at these locations were imaged and observed. Again, 80nm, 100nm and 120nm lines and spaces were photographed and the results were compared. Here are the results:

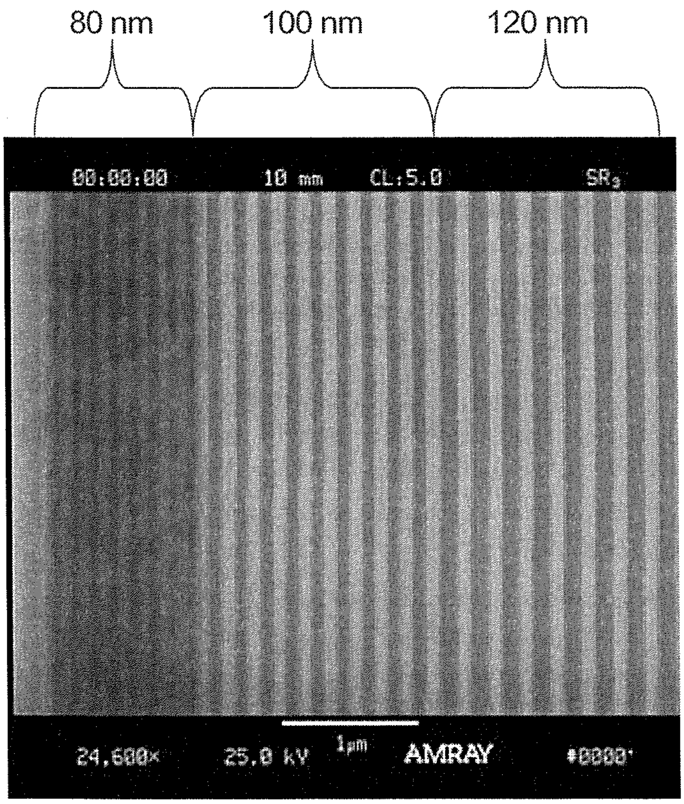

Figure 3: SEM Image (Baseline wafer, no soak)

This SEM image of the baseline serves as the 'control' image. The 100nm lines and spaces (l/s in the middle) are extremely straight and line edge roughness is very minimal. There is evidence of modulation in the 80nm region while the 120nm lines and spaces look very straight and clean.

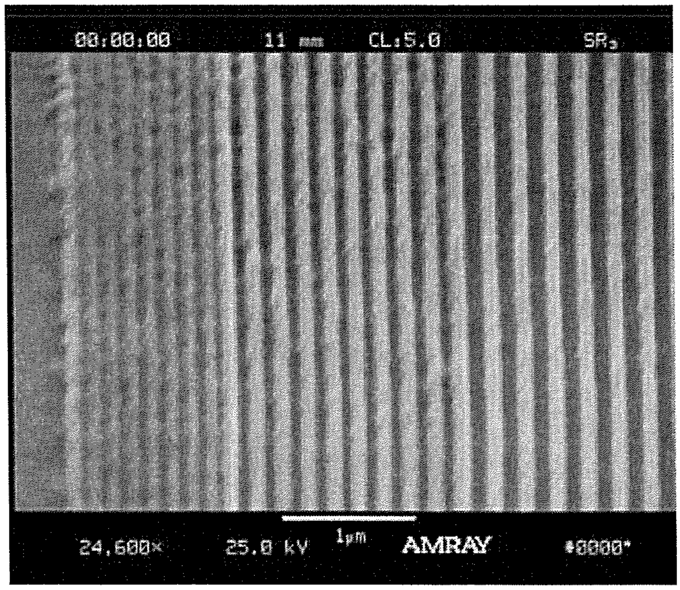

Figure 4: SEM Image (1min soak)

Compared to the baseline, the 1 min soaked wafer produced lines and space of 100nm very well. There is definite evidence of an increase in LER and a trend may be forming.

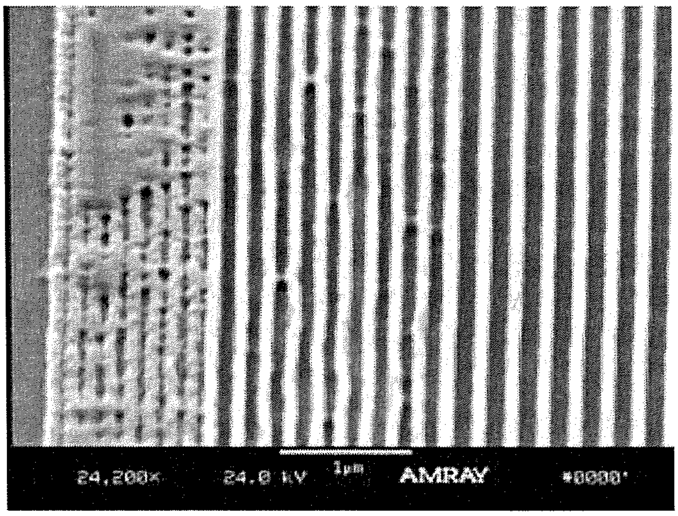

Figure 5: SEM (2min soak)

At 2min soak, the increase in LER is more and more evident. There are evidences of some micro-bridging which refers to lines that form a bridge over a space separating them. This is normally due to an excess of T-topping (amine contamination causing the top of lines to form a 'hat' or a crust which looks like the letter T from a cross-sectional view) and contamination. 120nm lines and spaces are extremely straight and have very low LER. The 100nm lines and spaces do not compare perfectly with the baseline thus adding to a possible trend of increasing LER due to the soak in water.

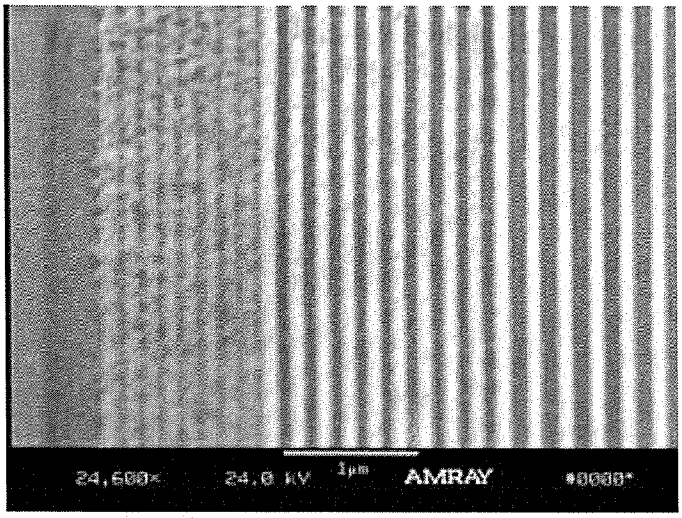

Figure 6: SEM (4min soak)

Above is a SEM image of the 4min soaked wafer. Here, it is clear that the 100nm lines and spaces compare very closely to the baseline wafer. The LER is extremely low and there are no signs of T-topping or micro-bridging. At this point, it was possible to make the observation that the water has minimal effects on the quality of imaging. However, at a short 4min soak, it was inadequate data to make any strong conclusions on the effects of water. The trend of increasing LER due to the water soak had to be further verified by studying longer soak times. Images at 8min, 16min and 32min had similar qualities to images taken previously. However, the most important result was the 64min soaked wafer. After a long soak of over an hour in H_2O, poor image quality was expected. SEM images were taken at the exact same location as the other soak times and the results were phenomenal. The SEM image below shows the quality of the image is extremely high contrast and no signs of degradation are evident.

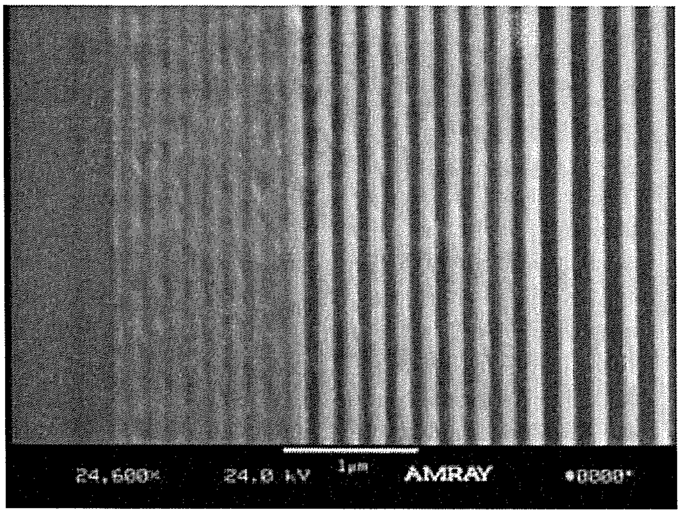

Figure 7: SEM (64min soak)

Here, the resolution of 100nm lines and spaces is very good and there are minimal LER. The jagged appearance of the lines and spaces is due to small vibrations during SEM imaging. Through investigating additional images at the 64min soak time, it was possible to conclude that the 100nm lines and spaces are identical to the lines and spaces of the baseline wafer.

V. CONCLUSIONS

After initial analysis of results, it was possible to conclude that good imaging of 100nm lines and spaces can be achieve for different soak times up to 4 min past one hour. Further soaking results were not obtained in this project. The ability to resolve 100nm lines and spaces after a whole hour of soaking in water prior to exposure is a great result. This range of soak time covered any amount of time the water may be in contact with the photoresist prior to exposure. Although the EXITECH system is not ready to expose the entire wafer (6" or 8"), the hour simulation of water to photoresist contact should have simulated any possible prolonged contact.

These results are very beneficial to any further work with the EXITECH system since it has verified imaging capability for up to an hour of water contact with photoresist. However, the results obtained here in this project are only qualitative results. Future work with this project may help identify unknown sources of LER and film degradation. Possible works include chemical analysis of the water after certain soak times. This kind of analysis will help determine if any of the chemicals from the photoresist such as PAG (Photo Acid Generator) has leached into the water. If such results can be obtained, then the percentage of PAG loss during soaks can be determined and calculated. These kinds of effects may result in alterations in the properties of water, which is critical in Immersion Lithography.

Also, further SEM analysis of the results can be performed in order to view cross-sectional profiles which will reveal any other effects of water. Sidewall angle decrease/increase can be used to determine the interaction between water and photoresist.

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James H. Park (DOB: June 28, 1980) Born in Rockford, Illinois into the PARK family. Started school in In-Chon, Korea and moved around many times before settling in Rochester, NY for University. Attended public schools in New Jersey and international schools in Jakarta, Indonesia (JIS) and New Delhi, India (AES). Arrived in Rochester, NY in the summer of 1999 and have been attending RIT since then. Currently working for Dr. Bruce Smith in Immersion Lithography research with the EXITECH System.