

Immersion Lithography: Moving Microlithography to Nanolithography

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Microlithography has been the primary process for integrated circuit (IC) manufacturing over the past several decades. In this process, Figure 1, a silicon wafer is spin coated with a polymer based film known as a photoresist. Portions of the film are then exposed to UV radiation of a particular wavelength through a partially chrome-plated quartz mask. The chrome plating on the quartz outlines a 2-D circuit design. Small molecules in the resist film, photoacid generators (PAGs), undergo a reaction in the exposed regions to produce acid molecules. These acids are used to catalyze a solubility-switching reaction in the polymer during a post exposure bake. This renders the exposed areas soluble in an aqueous base solution which is used to remove the polymer in these regions and leave a positive tone image of the circuit design. Subsequent etch and strip steps are then used to transfer the pattern into the silicon and remove the remaining resist material.¹

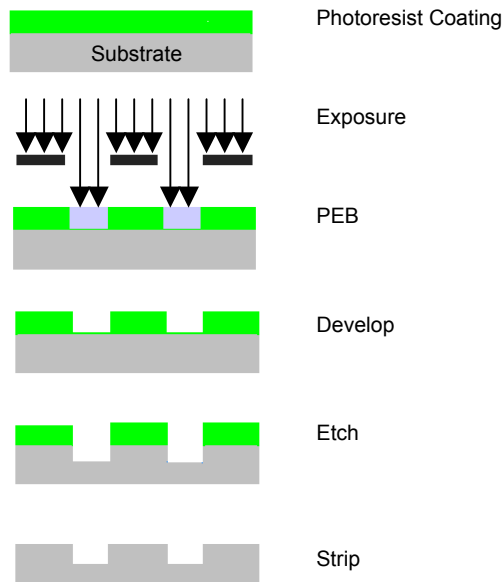


Figure 1. Illustration of positive tone microlithography process.

While the basic lithographic process has remained relatively unchanged for several decades, advances toward printing smaller features with lithography have been made. Traditionally, these advances have resulted from the development of new sources of UV radiation of smaller wavelength. With each step down in wavelength, new optical systems and resist materials have had to be developed.² Because of the ever increasing costs for such development and implementation into manufacturing, an alternative lithographic process has been proposed. This process, known as immersion lithography, was first proposed in the 1980's and has recently been revived.^{3,4,5} Immersion lithography is now considered the most likely candidate for printing 65nm features with 193nm optical lithography.⁶

Immersion lithography incorporates a liquid medium with an index of refraction (RI) higher than air into the gap between the final lens element of an exposure tool and the photoresist-coated silicon wafer. Currently, pure water is seen as the best candidate for an immersion fluid with 193nm lithography because of its high RI and low absorbance.^{7,8} The higher RI of the liquid acts to better focus the exposing radiation into the photoresist according to Snell's Law, Equation 1 and Figure 2. In addition to the improvement in focus to existing systems, immersion lithography also enables the development of new lens systems with better resolution than would be possible with dry 193nm lithography. With these potential improvements, the immersion process has raised questions about both the interactions between water and current lithographic materials and whether further improvements in focus and resolution would be possible. This work addresses both issues with various experimental and simulation methods.

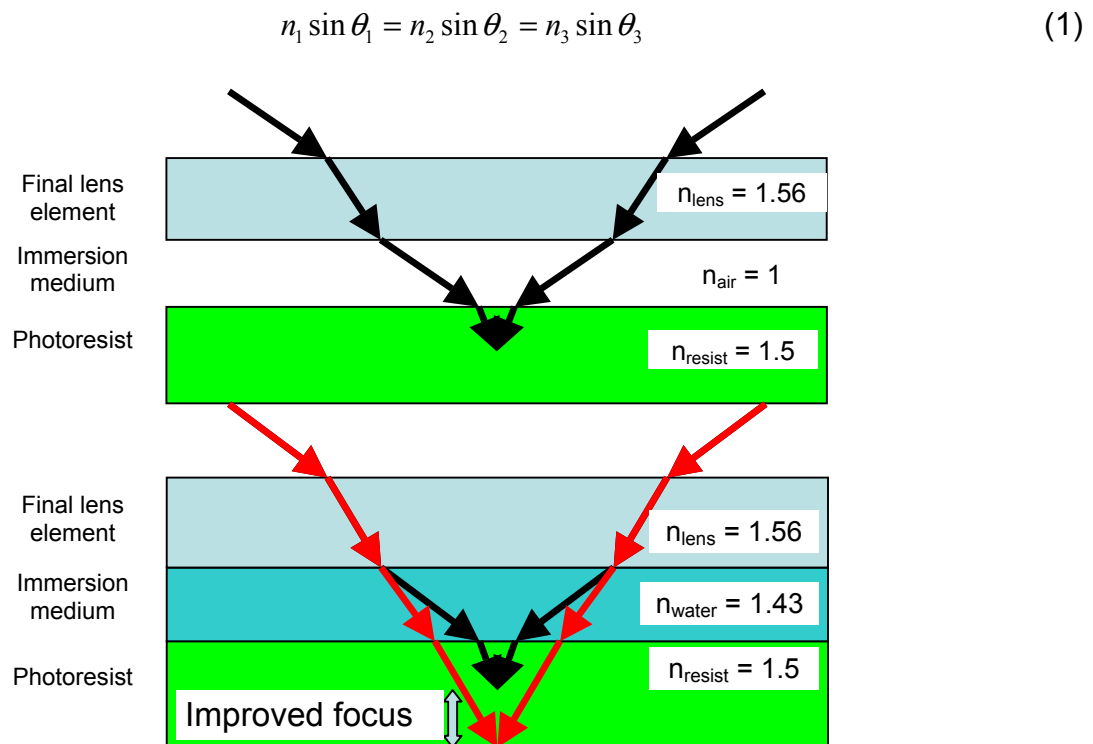


Figure 2. Ray tracing of exposure radiation through film stack representing lens, immersion medium and photoresist.

The intimate contact between the lens, water and photoresist raised the possibility of small molecule resist components – residual casting solvent (RCS), PAGs and base quenchers – being leached from the film by the immersion water. This could lead to contamination of the lens and/or degradation of the resist performance. To address this issue, an extremely sensitive measurement technique was needed to quantify the small amount of extraction expected. Therefore, a radiochemical analysis was developed to provide high sensitivity, precision and selectivity. For this analysis, a typical casting solvent and a PAG were synthesized with a carbon-14 containing precursor. The resulting radiolabeled resist components were then individually incorporated into model 193nm resist formulations, provided by resist vendors TOK (Japan) and AZ Clariant (Somerville, NJ). Films of these resists were cast onto 2in Si wafers and immersed in deionized water for 30sec to 30min. The

immersion water was then counted using liquid scintillation counting to determine the amount of each component that was extracted. A blank sample was also counted to determine the background noise level. The results of these measurements are shown as the counting rate, counts per minute (CPM), in Figures 3 and 4.

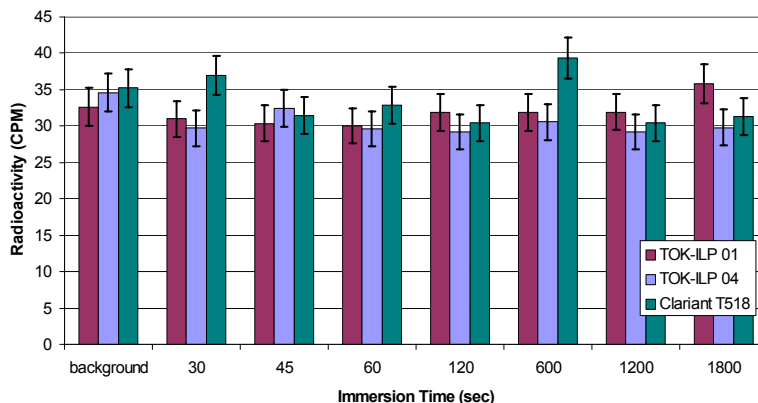


Figure 3. Radioactivity from ¹⁴C-RCS in immersion water vs. immersion time.

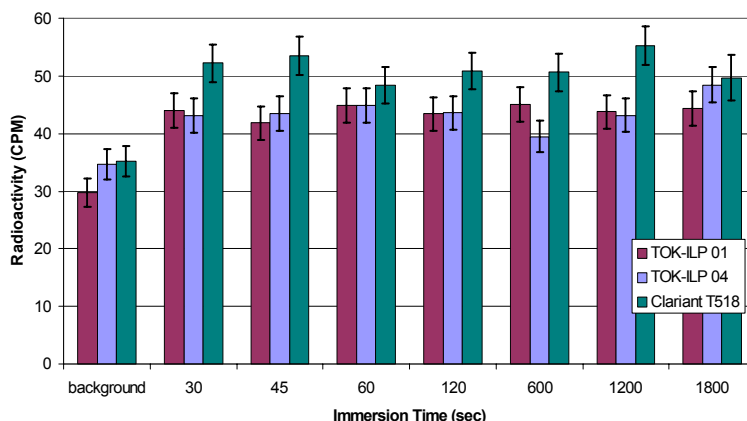


Figure 4. Radioactivity from ¹⁴C-PAG in immersion water vs. immersion time.

The measurements of immersion water placed on resist films containing labeled casting solvent show that no statistically detectable, above background, amount of RCS was extracted in 30min. However, the results from the ¹⁴C-PAG experiments show that a small, but detectable, amount of PAG was extracted. The extraction was evident after 30sec of immersion, and the amount extracted did not increase with immersion time. To confirm this, the experiment was repeated with a 30sec prerinse before immersion. Figure 5 shows that the prerinse water contained a detectable amount of ¹⁴C-PAG comparable to the amount seen in Fig. 4, and that the immersion water did not contain any statistically detectable PAG. The amount of extracted PAG was determined to be approximately 40ng/cm², based the surface area of resist that was immersed.

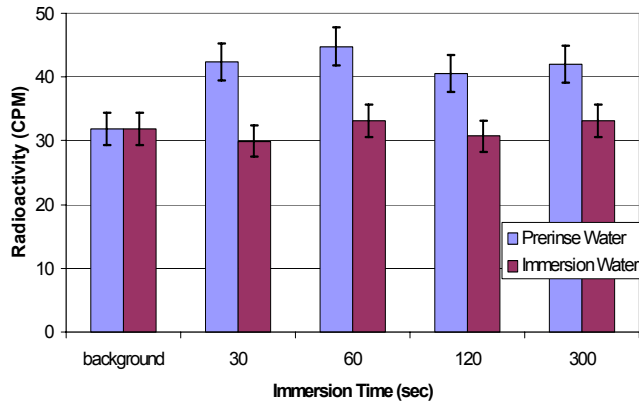


Figure 5. Radioactivity from ^{14}C -PAG in prerinse and immersion water vs. immersion time.

In addition to studying the interaction between water and photoresists, the potential of immersion lithography was explored. Using the lithography simulation program Solid-C[®], Sigma-C GmbH (Munich, Germany), the maximum process window for 90nm features was determined for both dry and immersion conditions. Figure 6 shows the increase in the depth of focus achieved with immersion with water.

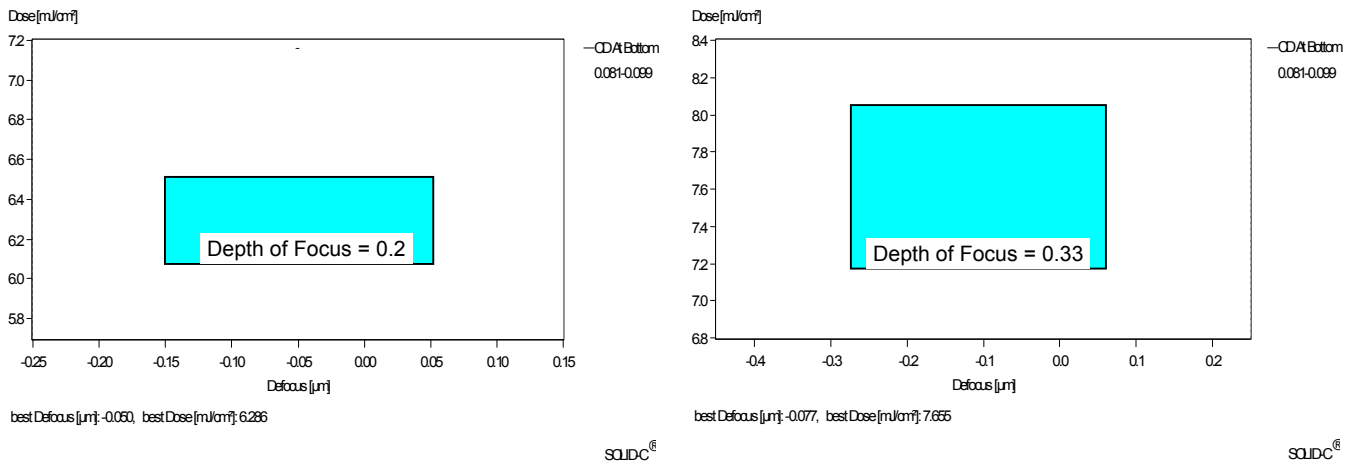
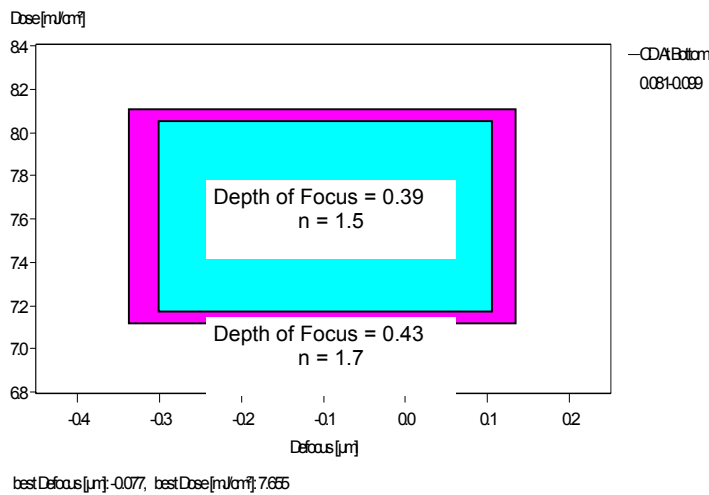


Figure 6. Process windows for 90nm features exposed under dry and water immersion conditions.

Further process window simulations showed that fluids with RI's higher than water resulted in even greater improvements to depth of focus, Figure 7.



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Figure 7. Process windows for immersion fluids with increasing RI.

Since the index of refraction of a medium is a material property, additives were proposed as a means to modify the RI of water. Solutions of inorganic salts were made and their RI's were measured using spectroscopic ellipsometry. Figures 8 and 9 show that aqueous solutions with inorganic salts greatly increased the index of refraction of water. Figure 8 illustrates the results of varying the cation of the salt. While using a larger cation resulted in a slight increase in the RI, it took a very large cation, tetraethylammonium (TEA), at a high concentration – 50wt% of TEA is approximately 3M – to achieve a significant change. However, Figure 9 indicates that the anion has a greater effect on the RI. Solutions with anions such as bromide, sulfite and thiosulfate have almost the same index of refraction. These results indicate that it would be possible to make aqueous solutions that would improve the potential of immersion lithography beyond what is expected with pure water.

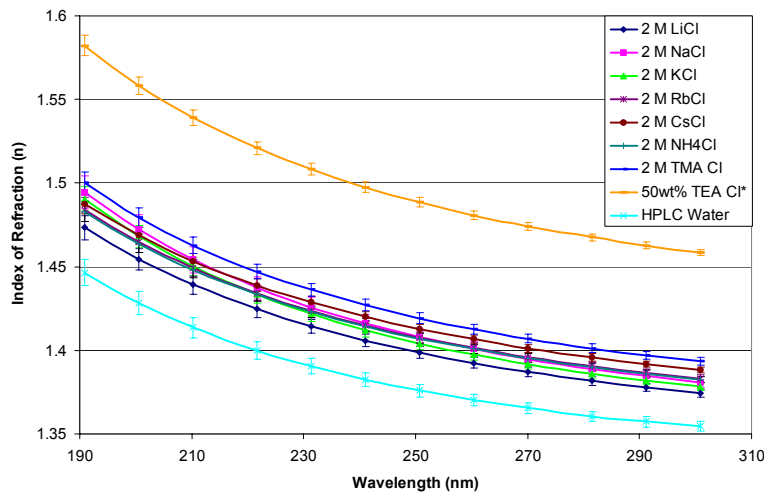


Figure 8. Index of refraction of aqueous chloride salt solutions vs. wavelength.

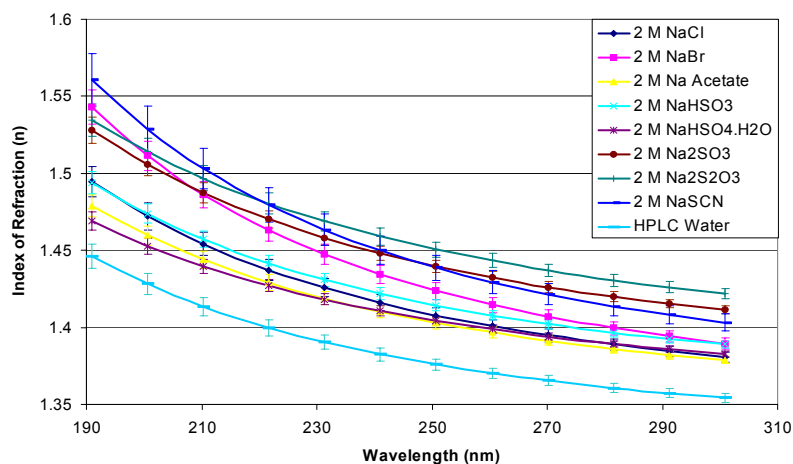


Figure 9. Index of refraction of aqueous sodium salts vs. wavelength.

This work has shown that water is essentially compatible with model 193nm photoresists. While no detectable amount of casting solvent was extracted from the resist films, a small amount of PAG was. This extraction can be avoided with a 30sec prerinse. The potential of immersion was also explored. It was seen that increasing the index of refraction of the immersion medium would result in further improvements to the lithographic process. Such high RI fluids are possible with water and ionic additives.

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