Extending Immersion Lithography with High Index Materials

Results of a feasibility study

by

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ABSTRACT

In this paper we report the status of our feasibility work on high index immersion. The development of high index fluids (n>1.64) and high index glass materials (n>1.9) is reported. Questions answered are related to the design of a high NA optics immersion system for fluid containment and fluid handling, and to the compatibility of the fluid with ArF resist processes.

Optical design and manufacturing challenges are related to the use of high index glass materials such as crystalline LuAG or ceramic Spinel. Progress on the material development will be reviewed.

Progress on immersion fluids development has been sustained. Second-generation fluids are available from many suppliers. For the practical use of second-generation fluids in immersion scanners, we have evaluated and tested fluid recycling concepts in combination with ArF radiation of the fluids. Results on the stability of the fluid and the fluid glass interface will be reported. Fluid containment with immersion hood structures under the lens has been evaluated and tested for several scan speeds and various fluids. Experimental results on scan speed limitations will be presented.

The application part of the feasibility study includes the imaging of 29nm L/S structures on a 2-beam interference printer, fluid/resist interaction testing with pre- and post-soak testing. Immersion defect testing using a fluid misting setup was also carried out. Results of these application-related experiments will be presented and discussed.

Keywords: Immersion lithography; 193nm lithography; High-n Immersion fluids; Immersion defects.

1. INTRODUCTION

The resolving powers of current optical exposure tools have reached 1.35NA using water-based immersion-fluid technology. High-n immersion technology may have the capability to extend optical lithography beyond 1.35NA. There is a window for this technology before production EUV lithography becomes available. High-n immersion lithography may potentially be initially used with single step patterning technology and, subsequently, with double patterning lithography for 32nm, 22nm and 16nm nodes.

To answer the questions associated with high-n immersion lithography, we embarked on a feasibility study, which evaluated the key technical challenges.

2. FEASIBILITY STUDY

For the high-n immersion lithography option, the key questions for the feasibility study are grouped in a number of study areas: Can we make a lens? Can we make an exposure system? Can we use high-n fluids? These areas are reviewed.

2.1 Can we make a lens?

Currently, the highest NA lens that is available is 1.35 for water-based immersion. Figure 1 indicates the development options for the optical design. The options highlighted are for numerical apertures of 1.45 and 1.55 using 2nd-generation immersion fluid, and 1.65 using a 3rd-generation immersion fluid. The 3rd-generation immersion fluids (n>1.8) are currently subject to significant development effort and candidate
fluids are being identified. These 3rd-generation fluids are not yet available, but 2nd-generation fluids are available.

The application of 2nd-generation fluids is limited by materials in the thin film stack between the wafer and the final lens element. For the water-based system, the limitation is the immersion fluid (water) \( n=1.44 \). Sin\( \theta \) for the aperture defining rays cannot physically be 1.0. A factor of 0.9 is possible. This gives a maximum NA of 1.35, limited by the water. Using the same calculation on a second-generation fluid (\( n=1.65 \)) gives a maximum NA of 1.55, as long as the fluid is the limiting refractive index in the thin-film stack. Currently, it is not. Quartz or calcium fluoride optical material in the final lens element have \( n=1.55 \) at 193nm, this limits the possible NA to 1.40, even with second-generation immersion fluids, unless the refractive index of the optical material in the final lens element is increased.

A possible solution is the use of BaLiF3 with \( n=1.65 \) for the final lens element, this allows the numerical aperture of the optics to be increased to the highlighted value of 1.45 (see Figure 1). Increasing the numerical aperture from the current 1.35 to 1.45 is only a 7% increase and is not considered to be enough to warrant the extensive development effort that would be required to bring on line the technology of a new class of immersion fluids and optical material. Attention is therefore focused on finding new final lens element optical materials that have refractive indices of >1.65. Figure 2 indicates the current state of progress.

Substantial progress has been made in this area by companies such as Schott. Schott reports\(^{(1,2)}\) development work on materials such as LuAG, sapphire, and ceramic spinel. LuAG has a refractive index of 2.1 and with low optical scatter. The concern with LuAG is optical absorption and birefringence (both intrinsic and stress). For LuAG, the main parameter under focus is the optical absorption value \( A_{10} \). This has been reduced to <0.2/cm and the target value is <0.003/cm. This must be improved by a factor of 50, this is a challenge, and has a long way to go. The outlook for significant further reduction, though, is good. The absorption level depends on levels of impurities. Impurity reduction is expected in areas such as the furnace, the crucible, and the starting materials. The preparation of proof samples is under way. Intrinsic birefringence for LuAG is measured at +30nm/cm. While this is higher than is desirable (<10 nm/cm) it is possible to compensate for it. Stress birefringence is currently <5nm/cm, and the target is <1nm/cm. There is optimism that the stress birefringence and homogeneity targets can be achieved with improved thermal control during crystal growing.

Work on backup materials such as ceramic spinel also show progress. Ceramic spinel has a refractive index of 1.92. Its current values of optical absorption is \( A_{10} <0.8 \) and the target value
$A_{10} < 0.003$. The biggest concern with the use of ceramic spinel is the optical scatter from the grain structure. This is a major issue.

For optical material, the developmental progress must be maintained. This is the most critical factor for high-$n$ immersion technology. An update on LuAG results is expected in March 2007.

The design of the optics with NA values of 1.55 is not expected to be a major problem. There is confidence that current designs$^{3,4}$ used for 1.35NA optics can be extended at least up to 1.56NA.

2.2 Can we make an exposure system?

An exposure system consists of a lens, a fluid-containment system (showerhead assembly) and a fluid-handling system. It is diagrammatically shown in block diagram form in Figure 3. The fluid handling concept now being explored consists of a fluid supply with a fluid purification (recycling) unit (being supplied by the fluid vendor).

![Fluid handling system](image)

Figure 3. Fluid handling system (fluid vendor sub-system)
The fluid supply unit interfaces with the exposure tool. It has storage units with fully integrated pumping, filtration, and fluid reconditioning sub-systems. The exposure tool has sub-systems to pump, control temperature, recycle, filter, and monitor the fluid as it is used in wafer exposure sequences. The fluid is constantly recirculating through the tool’s showerhead. Fluid is also circulated through the purification system to keep it within specific control limits. The role of the purification systems is to remove breakdown products that are the result of the photodecomposition of the fluid by the 193nm radiation. It is also required that any oxygen, which is a contaminant in the fluid, be removed because it reduces fluid transparency at 193nm wavelength.

2.2.1 High-n immersion fluid availability

Second-generation immersion-fluids have been available from multiple suppliers for about two years\(^5,6,7\). Figure 4 surveys the data. The availability of fluid samples has allowed the experimental addressing of questions about fluid contamination and degradation plus the development of fluid recycling technology.

<table>
<thead>
<tr>
<th>Spec</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
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<tr>
<td>refractive index</td>
<td>&gt;1.64</td>
<td>1.64</td>
<td>1.64</td>
<td>1.66</td>
<td>1.66</td>
<td>1.65</td>
<td>1.63</td>
</tr>
<tr>
<td>absorption A (10-based)</td>
<td>&lt;0.1/ cm</td>
<td>0.116</td>
<td>0.036</td>
<td>0.060</td>
<td>0.007</td>
<td>0.032</td>
<td>0.080</td>
</tr>
<tr>
<td>dn/dT</td>
<td>-500 ppm/K</td>
<td>-570</td>
<td>-550</td>
<td>-560</td>
<td>-570</td>
<td>-565</td>
<td>-565</td>
</tr>
<tr>
<td>viscosity</td>
<td>&lt; 0.003 Pas</td>
<td>0.0024</td>
<td>0.0033</td>
<td>0.0026</td>
<td>0.002</td>
<td>0.003</td>
<td>0.002</td>
</tr>
<tr>
<td>surface tension</td>
<td>~70 mN/cm</td>
<td>30</td>
<td>32</td>
<td>30</td>
<td>-30</td>
<td>-30</td>
<td>-30</td>
</tr>
</tbody>
</table>

Figure 4. Survey data of available high-n immersion fluids

In general, second-generation fluids have a refractive index of 1.64 +/- 0.1 (specification n >1.64) and absorption values at 193nm wavelength of A\(_{10}\) <0.04 (specification <0.10). Viscosity values are close to the specification value of <0.003 Pas. The fluids look very promising. The major concerns are the dn/dT (-550ppm/K) and the robustness of the fluid when irradiated with 193nm illumination.

Temperature coefficient is an issue because small changes in the fluid’s refractive index will induce significant aberrations to the imagery of the optical system. Image quality calculations show that the relatively high temperature coefficient of the fluids will require that the fluid temperature be controlled and stabilized to <1mK for a 1.55NA optics, when using second-generation immersion fluids. The feasibility study is aiming to demonstrate how well temperature of the fluid can be controlled. Currently no accurate measurements exist.

This control is thought to be possible, though difficult, to achieve. Figure 5 shows the rise in temperature sensitivity for Z9 and for Z16 aberrations as the numerical aperture is increased. The feasibility study identified a number of causes of temperature changes that must be controlled. The major ones are the evaporation of the fluid off the wafer/resist surface and the energy delivered by the imaging dose to the fluid. Compared to water, the new second-generation fluids have an 8 to 15 times
lower evaporation rate. To a large degree, the lower evaporation rate of the fluid compensates for its higher thermal sensitivity.

The heating effects of the exposing energy drives two specifications: the fluid absorption specification $A_{10}$ and the fluid flow rate through the showerhead. High flow rates move heated fluid quickly out of the optical path and limit the temperature deviation. High fluid absorption values drive up the exposure heat load.

\[
\begin{array}{|c|c|c|}
\hline
\text{Fluid} & 1.35\text{NA} & 1.55\text{NA} \\
\text{water} & 0.50 & 2.6 \\
\text{2nd gen fluid} & -0.073 & -0.43 \\
\text{df/dT} & -0.043 & -0.26 \\
\hline
\end{array}
\]

- **1.55NA system suffers from ~6x higher thermal sensitivity**

Figure 5. Optical aberrations induced by temperature changes in the high-n immersion fluid.

### 2.2.2 Showerhead and fluid containment

Showerhead design for the new fluids has progressed. A test stand is being used to develop new fluid showerhead and wafer system designs. Data graphed in Figure 6 compares the effect of scan speed on fluid containment with that of water. The contact angle data is plotted for the leading and trailing meniscus edges and for scan speed. Compared with water, the current second-generation fluids are very difficult to contain completely. Typically, scanning speeds of $>0.5$ m/s leave fluid behind on the resist-coated wafer. The graph shows a hysteresis effect between the leading and trailing edge contact angle. For water, this effect is quite

![Figure 6. Scan speed effect on fluid containment.](image)
large; for high-n fluids, the effect is much smaller. It is a surface-tension effect.

The scanning test results imply that full containment of high-n immersion fluids may not be possible at the high scan speeds used in lithography and therefore significant redesign of the fluid containment assembly will be required.

Typically, fluid is left on a wafer to dry. The residual fluid evaporates very slowly, >5 minutes. Initially, the resist is completely wetted by the fluid, but in less than a minute, the fluid film begins to break up into droplet patterns. After 3 minutes most of the droplets have evaporated.

It is assumed that the wafer surface will remain wet with the fluid and that the drying effects of fluid films are important. Figure 7 shows a typical drying sequence. It follows that the resist process must be insensitive to the fluid and that these drying droplets must not leave defects. The issue of fluid drying on resist must be studied.

![Fluid layer thickness increases with scan](image)

![Layer pulls back](image)

![Drops are formed](image)

![Drop dried, spots still can be seen](image)

Scan speed = 0.5 m/s

3 minutes

Figure 7. Typical high-n fluid drying sequence on a wafer.

### 2.3 Can we use the fluid?

Feasibility study testing of fluid drying on wafers has taken three forms: Droplets were sprayed onto pattern-exposed, resist-coated wafers; simple droplet drying tests; CD Uniformity test wafers were soak tested with fluid puddles.

#### 2.3.1 Fluid misting tests on wafers

The misting of fluid droplets onto a resist coated wafer is a convenient way to observe the drying effects of a wide range of fluid droplet sizes distributed over the entire resist surface. Misting tests on patterned wafers indicate that the second-generation fluids can give lower defects than with DI water. With these fluids it appears that the type of drying-mark defects that are typical of DI water are not present owing to the significantly lower PAG solubility rate in these second-generation fluids. In the initial experiments, it was found that the high-n fluid, as applied, was not yet clean enough. Drying tests on single droplets were therefore conducted so that the residues left by individual fluid droplets could be observed.
2.3.2 Droplet drying tests

In Figure 8, droplet drying test results are shown for a number of fluids from several suppliers. In general, the findings agree with the misting tests. It is observed that the fluids are not yet clean enough for high volume semiconductor manufacturing. Particulate defects, tarry skin residues, and crystalline deposits are all visible. The source of each of these is being sought. Leaching of plasticizer from tubing is suspected as is interaction with container materials and syringes. Particulates may be coming from fluid recycling columns. It is expected that the sources of these residues will be found and removed. A comparison of droplet drying in an air environment versus a nitrogen environment is also being checked in connection with the findings agree with the misting tests. It is observed that the fluids are not yet clean enough for high volume semiconductor manufacturing. Particulate defects, tarry skin residues, and crystalline deposits are all visible. The source of each of these is being sought. Leaching of plasticizer from tubing is suspected as is interaction with container materials and syringes. Particulates may be coming from fluid recycling columns. It is expected that the sources of these residues will be found and removed. A comparison of droplet drying in an air environment versus a nitrogen environment is also being checked in connection with the observed skin formation.

Figure 8. Droplet drying tests

Figure 9. CD uniformity tests. Impact of fluid soaking on resist imaging
2.3.2 Critical dimension (CD) uniformity tests

CD uniformity test results are promising. Figure 9 shows typical results. A slight change in the mean CD (<2nm) for 70nm lines is normally observed. Experiments indicate that results depend both on immersion fluid type and on resist type. The results also indicate that the effect of the fluid on the resist differs between before and after exposure application. The application of fluid before the resist exposure tends to decrease the measured CD after development, while the application of fluid after resist exposure tends to increase CD after development.

The application of fluid both before and after exposure (similar to an exposure tool) tends to leave a slightly increased CD (1nm) over a dry control wafer. This is a similar value to that measured using DI water. Experiments on drying time versus CD uniformity indicate that the fluids must be adequately spin-dried before post-exposure bake.

It is also observed that these results are dependant greatly on the actual resist system and fluid combination. Good results were obtained with TOK6111 and with AZ2120.

Joint testing on different JSR resist was carried out. Results of contrast curves which were generated are shown in Figure 10. They show the different effect on the resist contrast of the pre- and the post-exposure fluid application. Contrast curve testing is attractive because the results are independent of focus and exposure uniformity effects.

![Normalized Contrast Curves of AM2073J](image)

![Normalized Contrast Curves of AR1682J](image)

Figure 10. Contrast curve effects for pre- and post-exposure HIL-001 soak tests on JSR resists.

2.4 UV hardness of high-n fluids

Part of the feasibility study to evaluate high-n immersion fluids examined its UV hardness. Fluid degradation and optics contamination were examined. Figure 11 shows the test apparatus used for the measuring of fluid absorption and for irradiating of the fluid in a flow cell with laser illumination. Fluid samples are being supplied at regular intervals by vendors, particularly DuPont. Exposure to 193nm illumination degrades the fluid and increases absorption. Figure 12 shows typical experimental results for the UV irradiation of second-generation fluids (DuPont IF132). Fluid absorption at 193nm wavelength is monitored using a special metrology fluid cell. This metrology cell has three path lengths for the fluid so that by simple subtraction, the impact of the quartz windows on the cell transmission can be removed. An active recycle package supplied by the fluid vendor purifies the fluid during the irradiation cycle and reduces the fluid degradation rate significantly by removing breakdown radicals. Figure 12a indicates the place on the graph at which oxygen absorbed in the fluid is being removed. Also shown is the point at which the fluid recycle package is turned on. Once the absorption of the fluid has been stabilized and measured, the laser irradiation of the flow cell at 6.8mJ/cm² is turned on and the degradation rate of the transmission for the flow cell recorded. In this test, 10,800secs is equivalent to 24hrs on a Twinscan system.
Figure 11. Fluid irradiation and absorption measurement test apparatus

A typical transmission results for an irradiated flow cell is shown in Figure 12b. The results indicate a build-up of residues on the cell windows that is a non-linear function of laser pulse energy. It is observed that the flow cell darkening rate increases rapidly with the laser pulse energy. The window darkening rate for the front window in the flow cell appears to be independent of the fluid transmission status. Used fluid contaminates the window at approximately the same rate as fresh, new, highly transparent fluid. The window contamination rate is dependant upon fluid flow rate.

For the fluid flow conditions used in the reported experiment, the transmission loss can be as low as 1% for the equivalent of 24hrs run on a Twinscan system.
Experiments on the cleaning of windows have been conducted. Cleaning processes that are effective in removing residues from irradiation have been developed. Nevertheless, optics contamination has been identified as a major issue and is being fully characterized so that rates can be reduced.

2.5 Imaging

Imaging is a key component of the feasibility study. Resist cross-sections of 100nm lines taken from CD uniformity testing is shown in Figure 13. There is essentially no significant difference in resist profile between the soaked resist imaging and the dry imaging.

Tests using an interference imaging test stand\(^{(9, 10)}\) demonstrate that 29nm L/S printing is available with second-generation fluids on currently available chemically amplified resists (effective numerical aperture was 1.64, using fluid with n = 1.65). Figure 13 shows typical 29nm L/S results. The resists do have line edge roughness (LER), but this is generated by the chemistry of chemical amplification, rather than by any interaction with the second-generation immersion fluid. Improvements in the engineering of the resist are expected to reduce line edge roughness.

The interferometer test stand is also being used in the assessment of third-generation immersion fluid candidates. Path lengths in the fluid have been shortened to accommodate higher fluid absorption. To date, no candidate fluids have been available with measured refractive index that exceeds 1.73, and even these fluids are currently too absorbing to test. Progress on third-generation fluids and on the development of high-n resists\(^{(11)}\), which will be required to gain the full potential of a 3rd-generation fluid, is slow but ongoing.

![Image](AM2073J Dry Control)

**Initial results with Dupont IF169 (gen2 fluid)**

(29nm L/S, \(N_A^{\text{effective}} = 1.64\))

![Image](AM2073J Exposed To HIL 001)

**LS using an interference set-up**

85 nm ARC-29A, 50 nm PARIM850 resist

Figure 13. Imaging results with second-generation fluid: CD uniformity resist profiles for 100nm lines; and 29nm L/S using an interference printer (\(N_A^{\text{effective}} = 1.64\)).

2.5 Imaging simulations

Simulations of the performance of a 1.56NA imaging system are shown in figure 14. They indicate that a good process window is possible for 32nm L/S imaging using aggressive low-k image enhancement techniques. Depth of focus of over 0.8um is possible with an exposure latitude at best focus of 20%. Aggressive polarized dipole illumination is used with special attenuated phase shift masking.
3. SUMMARY AND CONCLUSIONS

The feasibility study is producing a wide range of results. Figure 15 summarizes them. Many areas of

- Can we make the lens?
  - Hyper-NA optical system design
  - High refractive index glass availability
  - IBR compensation methods

- Can we make the system?
  - Fluid containment (immersion hood)
  - Scanning tests & thermal control
  - Fluid recycling system

- Can we use High Index fluids?
  - Radiation hardness of fluid
  - Optics contamination
  - Resist interactions
  - Defects on resist
  - Resist profiles and line edge roughness
  - Exposure latitude
  - Supply of second-generation fluid from vendors
  - Supply of third-generation fluid from vendors

Figure 14. Depth of focus and process window simulations for 32nm L/S using aggressive low-k techniques

Figure 15. Feasibility study summary
technical challenges listed are deemed to be feasible; some are obviously more feasible than others. Three areas that could currently represent showstoppers are indicated: availability of optical-quality high-n final lens element material; optical surface contamination rate from the UV irradiation effects on the immersion fluid; the lack of availability of third-generation immersion fluid (this limits the extendibility of the technology). All three of these areas are being worked on and could become feasible. High refractive index optical material proof samples may be available within the next 6 months. Experimentation with optical surface contamination mitigation is ongoing. The results in all areas are encouraging enough to continue the feasibility study.

3.1 Outlook

There is an opportunity for second-generation immersion at 34nm half pitch. Second-generation fluid can extend single exposure immersion lithography toward 32nm node. In the longer term, this high-n immersion technology may allow the extension of double processing lithography to past the 22nm node. The window of opportunity is between the availability of new high-n final lens element material and the onset of production EUV lithography. It is expected that the primary application would be for the Logic sector.

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