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# High Index 193 nm Immersion Lithography: The Beginning or the End of the Road

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## ABSTRACT

For several years, SEMATECH has invested significant effort into extending 193 nm immersion lithography by developing a set of high index materials. For high index immersion lithography (HIL) to enable 1.70NA imaging, a high index lens element with an absorbance < 0.005/cm, a fluid with an index of  $\ge 1.80$ , and a resist with an index >1.9 are needed. This paper reviews the success or failure of various HIL components and presents the top final material prospects and properties in each category.

Since this abstract was submitted, the industry has decided to cease any effort in HIL, not because of fundamental showstoppers but because of timing. This choice was made even though the only currently available technology the can enable 32 nm and 22 nm manufacturing is double patterning. This may represent a paradigm shift for the semiconductor industry and lithography. It may very well be that using lithography as the main driver for scaling is now past. Due to economic forces in the industry, opportunity costs will force performance scaling using alternative technology.

Keywords: Immersion lithography, High refractive index, High NA imaging

# **INTRODUCTION**

During the past three years, high index 193 nm immersion lithography was considered a potential extension to the current water-based 193 nm immersion lithography. As the industry progressed through the most recent technology generations, 65 nm half-pitch (hp) using 193 nm dry and 45 nm hp using 193 nm water immersion, it was unclear until recently how the 32 nm hp generation would be supported. While extreme ultra-violet lithography (EUVL) has been the preferred technology from the standpoint of scalability, multiple technical and economic challenges have prevented the timely insertion of EUVL into high volume manufacturing (HVM) for either 32 nm or 22 nm. Additionally, when EUVL misses one more node the argument for scalability becomes less clear.

While high index immersion has been viewed as a further extension of 193 nm immersion and a possible solution to the lithographic requirements for 32 nm, the development of double patterning (DP) technologies has gained traction and could be used to extend the technology to 22 nm and perhaps beyond. DP technologies include numerous process variations, including spacer technologies, Litho-Etch-Litho-Etch (LELE), and Litho-Freeze-Litho-Etch (LFLE), which satisfy the target feature sizes and geometries. In fact, recent device work<sup>1,2</sup> has shown the ability of DP to supersede EUVL from a device scaling and performance point of view. This new "lithographic" approach represents a wholesale change in scaling for the industry, which is being driven far more by processing than by introducing new lithography hardware. The adoption of "processing lithography" opens other doors to "performance scaling" that are not driven by lithography but simply by opportunity costs.

High index immersion remains a potential lithographic solution to further complement and extend the applications of DP technologies to smaller dimensions or relaxing  $k_1$ .<sup>3</sup> The high-index current status and development challenges are discussed below.

#### The High Index Extensions to Immersion Lithography

Projection lithography is based on the projection of a demagnified image of a mask as an aerial image at the wafer surface. Traditional projection lithography has resolution limits set by the Raleigh equation,<sup>4</sup>

$$R = k_1 \frac{\lambda}{n \sin \theta} = k_1 \frac{\lambda}{NA} \tag{1}$$

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The steady reductions in wavelengths ( $\lambda$ =436 nm, 365 nm, 248 nm, 193 nm) have been accompanied by increases in the numerical aperture (NA) of optical systems to reduce resolution. The k<sub>1</sub> factor has also been reduced through various illumination configurations to improve resolution with a given system of wavelength and NA. Table 1 shows the k<sub>1</sub> values for several target hp features with systems of varying NA for both single- and double-patterned processes.

In the simplest case, air fills the gap between the last lens element of the projection optic and the resist-coated wafer. With air in the gap, the NA is inherently limited to 1.0, with a practical limit of 0.93. Immersion lithography is the first extension to traditional projection lithography, replacing the air in the gap with water. The achievable NA, is equal to nsin $\theta$ , and is limited to a fluid refractive index of 1.44 for water, with a practical NA limit of 1.35. Over the past five years, immersion projection systems have quickly developed from concept to the practical limit of 1.35NA in current state-of-the-art production scanners. Water immersion is considered the first generation of immersion lithography.

		65nm	57nm	50nm	45nm	40nm	36nm	32nm
k₁ for	1.30NA	0.438	0.384	0.337	0.303	0.269	-	-
Standard	1.35NA	0.455	0.399	0.350	0.315	0.280	0.252	-
hp features	1.45NA	0.488	0.428	0.376	0.338	0.301	0.270	-
•	1.55NA	0.522	0.458	0.402	0.361	0.321	0.289	0.257
	1.70NA	0.573	0.502	0.440	0.396	0.352	0.317	0.282

Table 1. k<sub>1</sub> values for various imaging systems and half-pitch technology nodes.

		32nm	28nm	25nm	22nm	20nm	18nm	16nm
k₁ for	1.30NA	0.431	0.377	0.337	0.296	0.269	-	-
Double-patterned	1.35NA	0.448	0.392	0.350	0.308	0.280	0.252	-
hp features	1.45NA	0.481	0.421	0.376	0.331	0.301	0.270	-
•	1.55NA	0.514	0.450	0.402	0.353	0.321	0.289	0.257
	1.70NA	0.564	0.493	0.440	0.388	0.352	0.317	0.282

The development of the optical material for the last lens element of the projection optic became a limiting issue to the NA, in tandem with the organic immersion fluids. Assuming the successful development and integration of these materials, the practical limit of a projection optical system would be approximately 1.55NA. This translates, if manufactured, to producing 32 nm hp features at an aggressive  $k_1$  of 0.257, with  $k_1 = 0.25$  as the optical limit.

The subsequent generation of immersion lithography materials was projected to be a system to deliver 1.70NA with 32 nm hp imaging at a slightly less aggressive  $k_1 = 0.282$ . The requirement for the fluid index was therefore defined at  $n\sim1.80$ . However, neither current fluid advancements nor the projection of fluid advances could enable this degree of index enhancement due to fundamental limitations. Additionally, increasing the fluid index to 1.80 created unique anti-reflection issues in simulations, requiring the refractive index (RI) of the resist, commonly 1.67–1.72 for 193 nm resists, to maintain a value equal to or greater than the fluid index for proper pattern formation. This issue was initially discussed by McIntyre et al.,<sup>5</sup> but has not yet been confirmed experimentally due to the lack of materials.

### HIGH-INDEX MATERIAL STATUS

#### **High Index Lens Material Development**

The final lens element in a high index system must satisfy several stringent requirements. It should have a sufficiently high RI (n> 1.7 at 193 nm), sufficiently low absorption coefficient (<0.005/cm, base 10), and sufficiently low intrinsic birefringence (< 10 nm/cm). From extensive early materials studies,<sup>6</sup> the candidate material with the best chance of meeting such requirements is lutetium aluminum garnet, Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>. BaLiF, developed by Tokuyamar<sup>7</sup>, was also a potential candidate for a 1.55 NA optical system, but with only a moderate increase in RI up to 1.64 at 193nm (relative to quartz RI of 1.56), BaLiF lacked the extendibility to 1.70 NA commercialization. LuAG, however, has a RI of 2.14 at 193 nm with sufficient extendibility. The fundamental bandgap of the material is ≈6.9 eV (180 nm), well below 193 nm.

The intrinsic birefringence is measured at 30 nm/cm, but can be compensated in the design of the projection optics. Even though fundamental LuAG absorbance at 193 nm should be sufficiently low, the best LuAG material at the time of the pre-screening study had an absorbance of 3.7/cm.

The aggressive development of lithography-grade LuAG material was launched at Schott Lithotec in 2005.<sup>8</sup> The goals of the program were to drive the absorption from  $\approx$ 4/cm to <=0.005/cm, at 193 nm and to increase grown boule sizes from less than 50 mm as in 2005 to 250 mm in diameter. Figure 1 shows the progress that was made over the three and one-half year span of the program. The absorption was improved by two orders of magnitude, down to 0.035/cm, by the fall of 2008. Absorption uniformity was demonstrated over crystals of up to 80 mm in diameter. The improvements were driven by purifying the starting raw materials and re-optimizing the crystal growing process.



Figure 1. Progress made at Schott Lithotec in improving absorbance of LuAG and scaling up boule sizes (from Reference 8)

#### Material Testing at MIT Lincoln Laboratory

Two batches of LuAG samples were tested at MIT Lincoln Laboratory during the material development program at Schott in an effort to address several materials questions:

Even though the measured sample absorption did not reach target specifications, was it possible to extract a fundamental absorption limit at 193 nm, separated from impurity or defect contributions?
 What was the durability of the material under long-term laser irradiation? Did 193 nm laser irradiation lead to any color center formation?

Figure 2 shows bulk absorbance of the two LuAG batches, which are a composite of four thickness measurements per batch. At 193 nm, material absorbances are 0.11 and 0.06/cm, base10, respectively, for both batches. These measurements were performed in a spectrophotometer with no surface cleaning. From previous work, material transmission at 193 nm can be enhanced by pretreatment with UV irradiation due to surface cleaning of adventitious hydrocarbons.<sup>9</sup> Indeed, for the LuAG samples measured here, subsequent laser irradiation showed an improvement in the measured bulk absorbance down to about 0.03/cm, for batch 2, in agreement with the lowest absorbance obtained by Schott Lithotee.<sup>8</sup>



Figure 2. Initial absorbance of two batches of LuAG material as measured at MIT Lincoln Laboratory as a function of wavelength.

To separate intrinsic absorbance from extrinsic contributions, we performed Urbach tail analysis.<sup>10</sup> In this technique, the absorbance of the material is measured down to the lowest accessible wavelength. The low wavelength (high energy) absorption tail is fit to the formula,

$$\alpha(h\nu) = \alpha_0 e^{(h\nu - E_0)/E_\nu} \tag{2}$$

where  $\alpha_0$ ,  $E_o$ , and  $E_v$  are the fitting constants. Extrapolation of this tail to the wavelength of interest—193 nm or 6.41 eV—represents the fundamental material absorption limit, whereas fit residuals represent an extrinsic tail due to defects or impurities.



Figure 3. Urbach edge fit of the two batches of LuAG material measured at MIT Lincoln Laboratory. Note that the absorbance scale is in the units of *"base e* per cm." See text for analysis details.

From the extrapolation of the Urbach edge fit from the two batches of LuAG material, the intrinsic absorbance is expected to lie between 0.001 to 0.003/cm, base 10, which is low enough to meet lithographic needs. Of course, experimental demonstration of this ultimate absorbance limit may not be trivial because of the aggressive purification required at all stages of the growth process.

Sample 193 nm irradiation was performed in our long-term laser exposure test-bed that has been described previously.<sup>11</sup> Samples were irradiated in a nitrogen ambient at 4000 Hz, 0.8 mJ/cm<sup>2</sup>/pulse. In situ transmission was assessed periodically. After a total dose of 0.5x10<sup>6</sup> J/cm<sup>2</sup>, no transmission degradation at 193 nm was observed. In fact,

for the most recently grown material, batch 2, substantial absorbance "bleaching" was observed by 0.03/cm, base 10, as was mentioned above. We, thus, do not expect that LuAG laser durability will be an issue for using the material in production.

#### **High Index Fluid Development**

As with a high index lens element, the development of a high index fluid was particularly challenging. The goal of reaching a refractive index of 1.80 at 193 nm is difficult alone, but it was coupled with the other stringent material requirements including an absorbance of  $\leq 0.25$ /cm, a viscosity of  $\leq 5X$  of water, a scatter limit of <0.2%/mm, a dn/dt upper limit  $\sim$ 300ppm, and a use lifetime of  $\sim$  one month. Making this task even more daunting was that very few variables could be exploited to increase the RI. If we examine the relationship shown in equation 3, it can be understood how we can fundamentally impact the refractive index of a non-polar or semi-polar organic fluid. Here,  $\eta$  is the absolute index of refraction, K<sub>d</sub> is the relative permittivity (dielectric constant), and K<sub>m</sub> is the relative permeability. It is a reasonable assumption that for all organic species K<sub>m</sub> will be approximately one, leaving K<sub>d</sub> the relative permittivity (dielectric constant) as the only way to dramatically affect the refractive index. The dielectric constant is a function of the density of a material and its polarizability. Although this relationship is an oversimplification and does not describe the behavior of a material versus wavelength, the latter can be extracted with the Kramers-Kronig relation.<sup>12</sup> Still, equation 3 indicates that changing the dielectric constant will result in a distinct change in the refractive index of a material.

$$\eta = \sqrt{K_d K_m} \tag{3}$$

Increasing the dielectric constant (i.e., density and or polarizability) of a chemical system can be accomplished through various means. Some of these are summarized in Table 2. For example, the trend is clear with respect to adding ever more polarizable groups. The addition of the larger halides results in a considerable increase in RI compared to the corresponding normal hydrocarbon. When adding F atoms to a species, the index decreases relative to the hydrocarbon. Even though the density increases with F substitution for say a hydrogen atom, the lack of polarizability of the F atom causes a net decrease in the RI. If additional methylene groups are added to any alkyl halide, as shown in the table, RI increases significantly, for example, going from methyl iodide to t-butyliodide. Clearly, adding any C<sub>n</sub>H<sub>2n</sub> reduces the RI dramatically. Also shown in the table is the impact of adding double or triple bonds on RI. Further, adding rings and aromaticity significantly increase the RI compared to analogous n-chain hydrocarbons. However, at 193 nm most of these moieties cannot be used due to high absorbance or reactivity.

Table 2 Some trends in RI with the introduction of constituents that impact polarizability.

Compound	RI (589nm)
$CH_3(CH_2)_4F$	1.360
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> Cl	1.412
$CH_3(CH_2)_4Br$	1.444
$CH_3(CH_2)_4I$	1.495
$CH_{3}I$	1.531
$(CH_3)CI$	1.491
n-Pentane	1.358
1-Pentene	1.372
1-Pentyne	1.385
n-C6H14	1.375
C6H12	1.426
C6H6	1.501

Over the past three years, the industry rapidly developed high index fluids with a RI of about 1.65 at 193 nm.<sup>13-16</sup> This achievement was no small task and enabled the development of 1.55NA-based lithography tools. However, the fluid required the semiconductor industry to shift from an aqueous to an organic 193nm immersion fluid. Although there were no fundamental showstoppers, the industry decided that the improvement in resolution, effectively a 14% improvement

extracted from equation 1, provided too little benefit for implementation by the industry. The industry generally agreed that if a fluid enabling 1.70 NA imaging was developed, that implementation would then be supportable.

The breakthrough that was made in high index organic fluids spurred a rush of research into other organic species that might have a higher index.<sup>17-21</sup> It was shown within eighteen months that fundamental limitations prevented the use of higher index pure organic fluids. There was also a flurry of work into alternative fluids such as organic salts and ionic liquids, but all of these systems had a least one material property and often more than one that disqualified their use as an immersion fluid.<sup>18, 21</sup> It became apparent that the only possible way to achieve the goal of a higher index fluid was to use a novel approach.

If we consider again how RI can be increased using polarizability and density, one can consider an inorganic species. These inorganic species could be dispersed as nanoparticles in a high index fluid enabling higher NA (>1.55) lithography. Although this may seem a daunting task, the real number of possible species is quite small. The material must first have a large bandgap to have any hope of having a transparency in the DUV. The candidate materials are  $Al_2O_3$  (sapphire), MgO, Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (LuAG), HfO<sub>2</sub>, and ZrO<sub>2</sub>. The Al<sub>2</sub>O<sub>3</sub> (sapphire) can be eliminated immediately due to the relatively low (1.92) index at 193 nm and the difficulty in maintaining the required material phase as a nanoparticle. MgO while attractive has a lower index than required for a 193 nm immersion fluid based on the fluid loading requirements derived from the Lorentz-Lorenz<sup>22</sup> formula as shown in equation 4. LuAG, with an index of 2.1 at 193nm, has been looked at by DSM Research, but a required 32 volume % (78 wt%) loading in decalin to achieve an index of 1.80 at 193 nm, seems unrealistic.<sup>20</sup> Additionally, because LuAG is a much more complex system than a binary oxide, it was removed from consideration. This leaves the group IVB oxides. The absorption cutoff for ZrO<sub>2</sub> is red-shifted 50 nm compared to HfO<sub>2</sub>, eliminating that species. Consequently the SEMATECH work focused on HfO<sub>2</sub> which made the task only slightly simpler. The RI of HfO<sub>2</sub> was measured to be approximately 2.90 at 193 nm,<sup>24</sup> a value that is consistent with the RI value of HfO<sub>2</sub> in the literature.<sup>25</sup> Additionally, the UV cutoff for the material is about 225 nm for the bulk, requiring a small blue-shift in the UV order for HfO<sub>2</sub> to be useful. A shift in the UV cutoff has been shown to be obtainable using a quantum confinement effect.<sup>26</sup> For example, in the case of ZnO, a UV shift of 100 nm was observed when reducing the nanoparticle size from 10 nm to 2 nm.<sup>26</sup>

Calculating the loading required to achieve the desired RI, based on equation 4,  $n_f=1.80$  (final refractive index) and  $n_s=2.9$  (transition metal oxide refractive index), we can estimate the volume fraction (Vs) of particles needed for this RI. A water-based fluid will require a volume loading of 37% nanoparticles to achieve a RI of 1.80. This may seem unrealistic when looking at a hard sphere contact model in solution; however, if we set a goal of 1.65 for the final aqueous based solution, which is the same for the current top organic candidates, the volume loading is then reduces to 22%. This is a number that may be obtainable for an aqueous based fluid. If, on the other hand, we start with a much higher index organic-based solution such as decalin at 1.65 or DuPont<sup>(tm)</sup> Immersion Fluid IF132, the volume loading becomes an even more reasonable, 19 volume %. These loading values, while theoretically possible, are clearly far from trivial. Notwithstanding, there is an additional benefit of structure packing for the material in solution that is not comprehended in a simple sphere packing model.. This structure packing efficiency has been described in detail by others, who state that a structure packing function will offer better material properties than the theoretical packing model, allowing higher loadings of the nanoparticles in fluids.<sup>27</sup>

$$\frac{n_f^2 - 1}{n_f^2 + 2} = V_s \frac{n_s^2 - 1}{n_s^2 + 2} + (1 - V_s) \frac{n_m^2 - 1}{n_m^2 + 2} \qquad (4)$$

The resulting fluids that have been prepared at SEMATECH supported Universities to date have had an aqueous fluid with a loading of about 18.5 vol % (69.8 wt%)) in water and 5 vol% in DuPont's IF132, which give extrapolated indices around 1.6 and 1.7, respectively. A 79.8 wt% aqueous solution has been prepared but has not been evaluated for RI. While the RIs of these fluids approach attractive numbers for both aqueous and organic fluids, a major effort in purification is still needed. For the commercially developed fluids, for example DuPont's IF132, major purification

efforts were required to enable viability as a 193 nm high index fluid. The fluids developed at Cornell and Columbia universities are now at the stage to require industrial purification. The basic synthetic route for obtaining the bulk of the nanoparticles investigated to date is quite simple.<sup>28, 29</sup> The difficulty in this technique is in the method required to prevent agglomeration of very small particles. This procedure has been summarized elsewhere.<sup>30</sup> The purification required to determine the true absorbance edge of these fluids is not possible in the university environment where the fluids have been produced. Dedicated equipment including glove boxes, preparation systems, pristine dedicated gas lines will all be required in order to reach required fluid purity. Further refinement will require additional resources and an industrial partner to obtain lithography-grade purity.

#### **High Index Resist Development**

In concert with the high index fluids development, work on a high index resist has been proceeding on several fronts. Simulations by several groups have described the benefit of reaching high RI values ( $\geq 1.90$ ). Driven by simulation results,<sup>31,32</sup> several groups have been aggressively working on increasing the RI of 193 nm resists,<sup>33-37</sup> The approach to resist development essentially follows the path for high index fluid (see above and equation 3). Much of the work has focused on incorporating heteroatoms into resist polymers to increase the polarizability and thus the RI. It appears that the preferred technique to increase the RI of the resist has been by introducing sulfur.<sup>33-37</sup> In fact, the options for increasing the resist RI are actually quite limited. For example, the addition of aromatic structures or larger halides (Cl, Br, I), which would all significantly increase the RI, are prohibited for 193 nm resists due to absorbance or photoinduced chemical reactions. So, too, is the use of many heteroatoms such as N and P in most forms prohibited, due to the basic nature of these species when introduced into a resist material. One of the means to introduce a transparent, nonbasic nitrogen is through a cyano moiety. Several of these cyano groups could provide transparency and help boost the RI. Increasing the structural rigidity of the polymer has also been attempted.<sup>33</sup> This approach actually works well in concert with the sulfur chemistry as the introduction of sulfur-containing monomers can balance the increase in the glass transition temperature( $T_{g}$ ) of the polymer caused by more rigid structures. However, work by several groups determined that there are distinct limits to how much sulfur can be incorporated into 193 nm type polymers without severely degrading the required resist properties.<sup>35, 36, 38</sup> Properties that degraded included the absorbance,  $T_g$ , and dissolution, all of which negatively affected the resists'imaging performance. Even in the best case, the highest refractive index obtained for a resist using sulfur approaches only about 1.80, far from the goal of 1.90. It also became clear that the RI did not increase as quickly as absorbance as would be expected with different functionalities of sulfur including the sulfides, sulfones, thioesters, and thoiethers. This result was also noted by Robert Allen's group at IBM.<sup>37</sup>

#### The Next Step on the Road to a High Index Resist

After October 2007, any mainstream work to increase the RI of resist had significantly diminished. The last remaining organization openly engaged in a high index resist effort was SEMATECH. It had become clear that, like the high index fluids, a simple organic system was not going to enable the high index goal to be achieved. Thus high index resist development followed the path taken by fluid development and incorporated high index nanoparticles. The proof of principle for using nanoparticles in resist had been demonstrated previously.<sup>39-41</sup> In that previous work, the material was added to promote transparency, not to increase RI. Since the starting point for the resist is an index of 1.7 only a loading of about 12 volume % nanoparticles will be will be requires.

Groups from Cornell and IBM collaborated to test the characteristics of the nanoparticles. Cornell supplied a samples of nanoparticles which IBM researchers cast into a thin film onto a wafer and measured them VUV-VASE. The results were recently published.<sup>37</sup> The film showed an absorbance of ~  $2.5/\mu$ m and a RI ~2.0. It should be noted that these nanoparticles contained some percentage of contaminating organic species and chlorine, which rasied the absorbance significantly and diluted the RI somewhat. Work is currently underway to eliminate the contaminating chlorine; however, even at this absorption level, it is clear that using these nanoparticles in current resist platforms to increase the RI is a reasonable approach. The nanoparticles have undergone additional purification, and resist evaluations indicate that no degradation occurs due to absorbance.

Currently, the progress stands at a loading sufficient to raise the RI of a 1.70 resist to about 1.75. The difficulty has been to functionalize the nanoparticles in such a way as to incorporate large amounts without affecting resist performance. Extensive details of this work can be found in a recent publication by Woo Jin Bae et al.<sup>42</sup>

#### Practical Imaging with High Index Materials

As with any new technology, the proof of concept—in this case the demonstration of 32 nm hp imaging with high index materials—confirms that the concept can work while still revealing any unanticipated issues.

At SEMATECH, 32 nm hp imaging has been demonstrated using 193 nm immersion interference lithography.<sup>43</sup> The Amphibian XIS system is an experimental microstepper that allows a reconfigurable optical system to incorporate various prism designs. The prism acts as the last lens in the optical system and has been interchanged with fused silica (quartz), BaLiF, sapphire, and LuAG prisms to demonstrate imaging. The optical configuration through the prism, the polished prisms for BaLiF and LuAG, and 32 nm hp imaging from the LuAG prism are shown in Figure 4.

Imaging tests with quartz, BaLiF, and LuAG prisms have yielded 32 nm hp imaging without issues. The sapphire prism, however, has been tested but has not yet produced quality imaging. A high level of absorption in the sapphire, a value yet to be quantified, may be contributing to flare, which has a demodulating effect on the interfering beams.





#### **Other Material Considerations**

To support the demonstration of imaging at 32 nm or beyond, resist stack optimization must be examined, since the stack plays a critical role in the image formation at the wafer surface. For 32 nm hp imaging, the effective NA is 1.50, and the incident angle approaches an aggressive 70° in the fluid, a significant anti-reflective concern. The design of the multi-layer

stack is highly dependent upon the refractive index and extinction coefficient (n&k) of the various component materials, including the bottom anti-reflective coating (BARC), the photoresist, and the topcoat (TARC). The BARC plays the most significant role in stack optimization. It is worth noting that stack optimization for 35nm hp features (1.38 effective NA) is much different than for 32 nm and therefore is not easily co-optimized with a single-layer uniform BARC. Graded or multi-layer BARCs may offer co-optimized solutions, but may also add to process complexity and cost.

While the TARC layer contributes to the overall anti-reflective strategy, its role in fluid meniscus control is also of interest in a production scanner. In water immersion scanners, defectivity issues have been linked to the fluid contact angle, since bubble defects are attributed to the advancing contact angle (ACA) and watermark defects are attributed to the receding contact angle (RCA). The static contact angle of water with production TARCs is approximately 80°, a fairly hydrophobic surface for water immersion. For prototype Gen2 organic fluids, the static contact angle is approximately 50° with the same TARC, not nearly hydrophobic enough for high speed scanners. Further developments in fluids, TARCs, and air curtains within the scanner could potentially contribute to system solutions.

#### CONCLUSIONS

In summary, HIL still offers a key opportunity to bridge the gap between the 45 nm and 32 nm half-pitch nodes. Additionally, 22 nm half-pitch imaging can be obtained with improved  $k_1$  using the combination of HIL and double patterning.

Lens material evaluation showed no transmission degradation at 193 nm after extensive dose exposure. In fact, for the most recently grown material, batch 2, substantial absorbance "bleaching" was observed by 0.03/cm, base 10, as was mentioned above. It is not expected that LuAG laser durability will be an issue for material use in production. A roadmap for further absorption reduction was provided but work ceased in October 2008 due to lack of industry support.

It has been determined that the successful production of a pure organic high index immersion fluid with a RI  $\ge$  1.8 is not possible because of fundamental limitations on how much polarizability and density can be introduced into organic molecules without significantly degrading their transparency. Additionally, absorbance/reactivity increase correspondingly in organics larger than decalin and organic fluids with heteroatoms.

The only remaining approach to achieving the high index required for > 1.55NA imaging is to incorporate dispersed nanoparticles into solution. It has been shown that a material with an index of 2.90 at 193 nm can be synthesized into nanoparticles of useful dimensions. Still, obtaining the required purity of the nanoparticles in solutions necessitates much work. Fundamental showstoppers such as scatter and viscosity have been eliminated. However, interactions of the nanocomposite with tools and surrounding materials (i.e., lens and resist) still must be exhaustively evaluated.

For a high index resist, simulations strongly indicate that a RI of 1.9 or higher will be required for the resist, assuming a RI of 1.8 for the high index fluid. The main effort toward obtaining the required size, quantity, and quality of the nanoparticles has been achieved. The path for incorporating high loadings of nanoparticles into 193 nm resist systems has been described and is currently under investigation.

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