Development of an Operational High Refractive Index Resist for 193nm Immersion Lithography

[1]Paul A. Zimmerman, [1]Jeff Byers, [1]Emil Piscani, [1]Bryan Rice, [2]Christopher K. Ober, [2]Emmanuel P. Giannelis, [2]Robert Rodriguez, [2]Dongyan Wang, [3]Andrew Whittaker, [3]Idriss Blakey, [3]Lan Chen, [3]Bronwin Dargaville, and [3]Heping Liu

[1]SEMATECH, [2]Cornell University, [3]University of Queensland
paul.zimmerman@intel.com

ABSTRACT

Generation-three (Gen-3) immersion lithography offers the promise of enabling the 32nm half-pitch node. For Gen-3 lithography to be successful, however, there must be major breakthroughs in materials development: The hope of obtaining numerical aperture imaging ≥ 1.70 is dependent on a high index lens, fluid, and resist. Assuming that a fluid and a lens will be identified, this paper focuses on a possible path to a high index resist. Simulations have shown that the index of the resist should be ≥ 1.9 with any index higher than 1.9 leading to an increased process latitude. Creation of a high index resist from conventional chemistry has been shown to be unrealistic. The answer may be to introduce a high index, polarizable material into a resist that is inert relative to the polymer behavior, but will this too degrade the performance of the overall system? The specific approach is to add very high index (~2.9) nanoparticles to an existing resist system. These nanoparticles have a low absorbance; consequently the imaging of conventional 193nm resists does not degrade. Further, the nanoparticles are on the order of 3nm in diameter, thus minimizing any impact on line edge roughness (LER).

Keywords: Immersion lithography, refractive index, photoresist, nanoparticles

1. INTRODUCTION

The introduction of water into 193nm lithography allowed its extension beyond the 45nm half-pitch node. The remarkable properties of water made 193nm immersion (193i) lithography a relatively quick and painless technology to develop compared to the significant materials challenges posed by immersion lithography options beyond water. The extension of immersion lithography to a second generation (Gen-2) may allow numerical apertures (NAs) up to 1.55[1-4] using a new lens material, lutetium aluminum garnet (LuAG), and a Gen-2 immersion fluid with existing resist materials. Organic fluids such as decalin and bicyclohexyl have refractive indices (RIs) in the needed range to complete the circle of materials. Although significantly different fluid handling will be required compared to water-based immersion lithography, no fundamental showstoppers exist for achieving Gen-2 immersion lithography. Gen-3 high index immersion lithography (HIL) offers an entirely new array of challenges from a materials perspective. The refractive index for all of the materials must be ≥ 1.8 to achieve a NA approaching 1.7 and thereby enabling imaging at the 32nm node.[5]

This paper describes a systematic approach to understanding the index requirements of photoresist to achieve 32nm node imaging. In addition, it describes the initial path for synthesizing a high index resist. Finally, this work lays out what is currently the most chemically feasible path for the creation of a commercial grade 193nm high index resist.

1.1 Simulations

To obtain a realistic target for the index of the resist material, several simulations were carried out to determine the most appropriate index value. This number cannot be viewed in a vacuum, however. Careful consideration must be given to the chemistry required to achieve such an increase in RI. Simply hoping for a specific RI is a "fool's errand" as the chemistry required is quite complicated. Additionally, the modification in chemistry must occur while still maintaining optimum resist properties.

PROLITH simulations were considered to model the likely performance of a resist in a Gen-3 1.70NA optical system to target 32nm line/space (L/S) features. Table 1 shows the simulation conditions used in PROLITH™ to evaluate the impact of the RI of the resist to the process window, depth of focus (DOF), and resist loss is shown in the subsequent figures. A fluid index of 1.80 was chosen as a likely target for the immersion fluid index. Other conditions were chosen to reasonably represent achievable targets for absorbance and diffusion. Resist index is the parameter under investigation.

Table 1 Outline of simulation conditions for determining values for high index resist

- Stepper
  - NA = 1.7
  - Source = Dipole 0.9s,0.1r
  - Azimuthal Polarization
  - Fluid n=1.8
- Mask
  - 32 nm L/S (64 nm Pitch)
  - attPSM 6%
  - Target CD = 32 nm
- Resist Model
  - Thickness = 70nm
  - Resist n = variable
  - Absorbance = 1.2um-1
  - Acid Diffusion = 10nm
  - Quencher Diffusion = 20nm
  - Quenching Fraction = 0.77*E0
  - Contrast = 8

Figure 1 shows the focus exposure matrix (FEM) (Bossung plots) obtained for resists with two different RIs. There is a subtle change with the resist index, perhaps too subtle to be viewed in this manner. It is obvious from Figure 2 that the process window loss from decreasing the resist RI is not catastrophic. Simulations were also used to extract the process window from the FEM. Figure 2 shows a side-by-side comparison for the FEM of a 1.75 and a 1.90 index resist. A clear difference is seen in the process window. Note in each case that the process window is limited by resist loss. The reason is that the critical dimension CD at the top of resist is out of focus compared to the bottom of the resist.
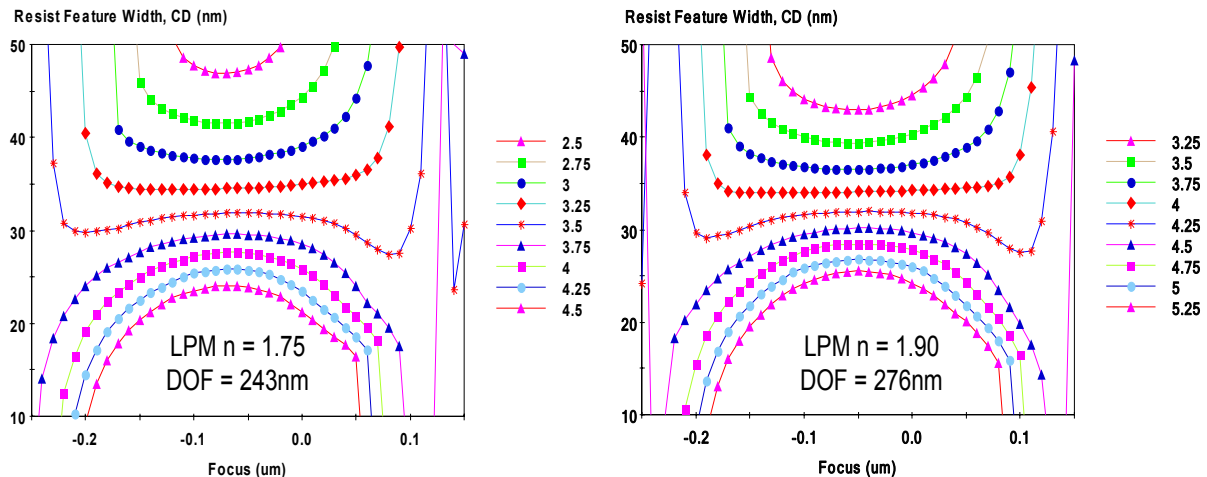

Figure 1 Focus exposure matrix obtained for resists with two different RIs showing a subtle change in the resist index (ECP)
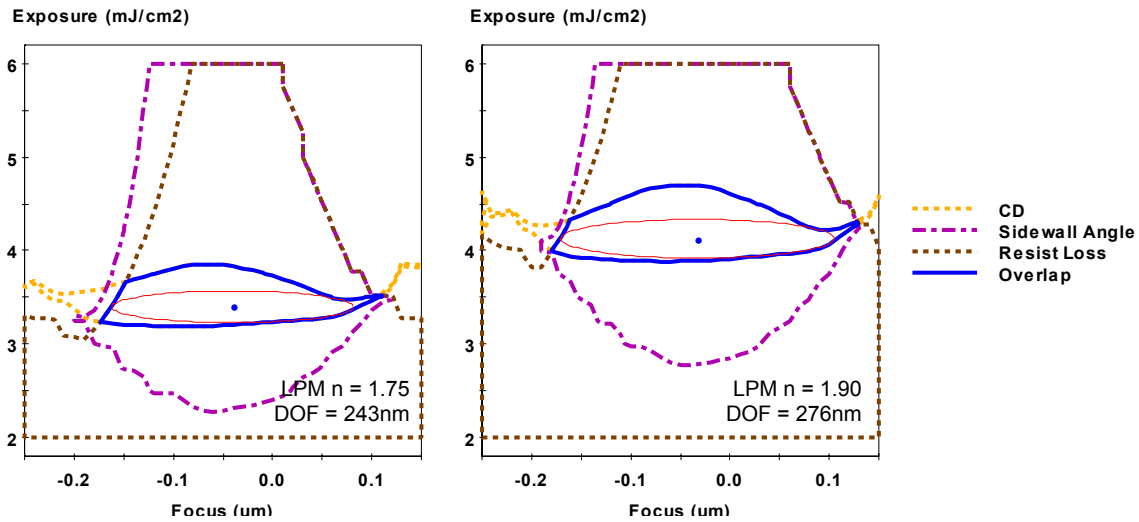
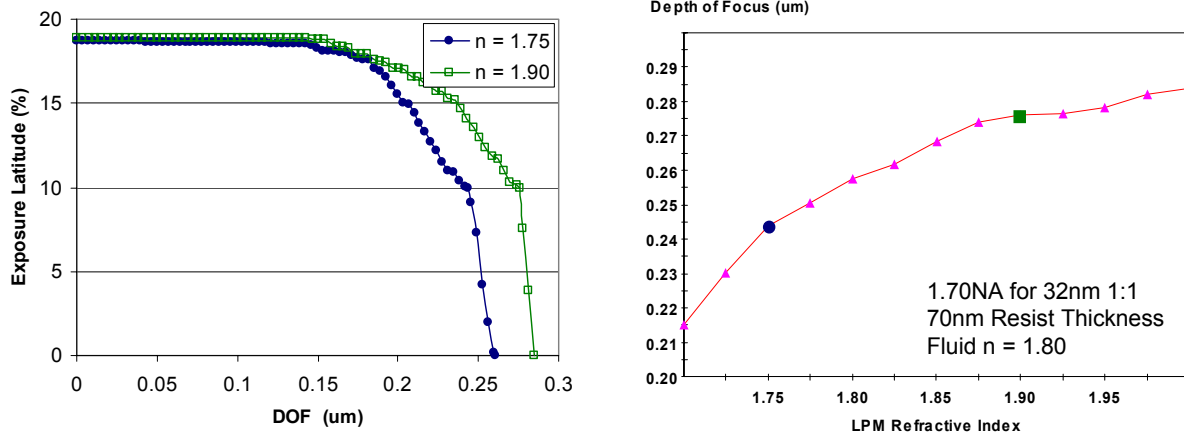Figure 2. FEM showing a side-by-side comparison of a 1.75 and a 1.90 resist index (ECP)

Figure 3A Exposure latitude as a function of DOF and 3B DOF at 10% EL vs. resist refractive index (ECP)

Normally, one will pick an acceptable exposure latitude (EL) for a given process and determine the DOF. This can be done for resists of different indices as shown in Figure 3. Figure 3A shows the EL vs. DOF for resists with refractive indices of 1.75 and 1.90. Figure 3B shows the DOF at 10% EL vs. refractive index. It is clear from the figure that considerable improvement in the DOF and process window can be achieved when using a higher index resist.

Using the DOF as the metric to optimize, increasing the resist refractive index is certainly one method. Other contributing factors to DOF improvement are the immersion fluid index and the resist thickness. As previously mentioned, the process window is limited by resist loss due to the top resist surface being out of focus relative to the bottom surface. Additional PROLITH simulations demonstrate an increased DOF with thinner resist. Figure 4 details the PROLITH modeling presented in sensitivity Plots for a resist index of 1.75 and 1.90, respectively. As observed in these plots, increasing the immersion fluid index and reducing resist thickness both contribute to an improved DOF. While there are diminishing returns for increases in resist index, both immersion fluid index and resist thickness exhibit fairly linear responses.

In practical applications, the resist thickness maintains an aspect greater than 2:1; therefore, a 70nm resist is reasonable for this discussion. Discussion of methods to reduce resist thickness while retaining pattern transfer is beyond the scope of this paper, but such methods represent further opportunities to improve the DOF. Figure 5A shows DOF as a function of resist index for various fluid indices. This plot further demonstrates the diminishing

response of the DOF as a function of resist index. The contour plot shown in Figure 5B demonstrates the DOF response for varying fluid and resist indices with a 70nm resist film.
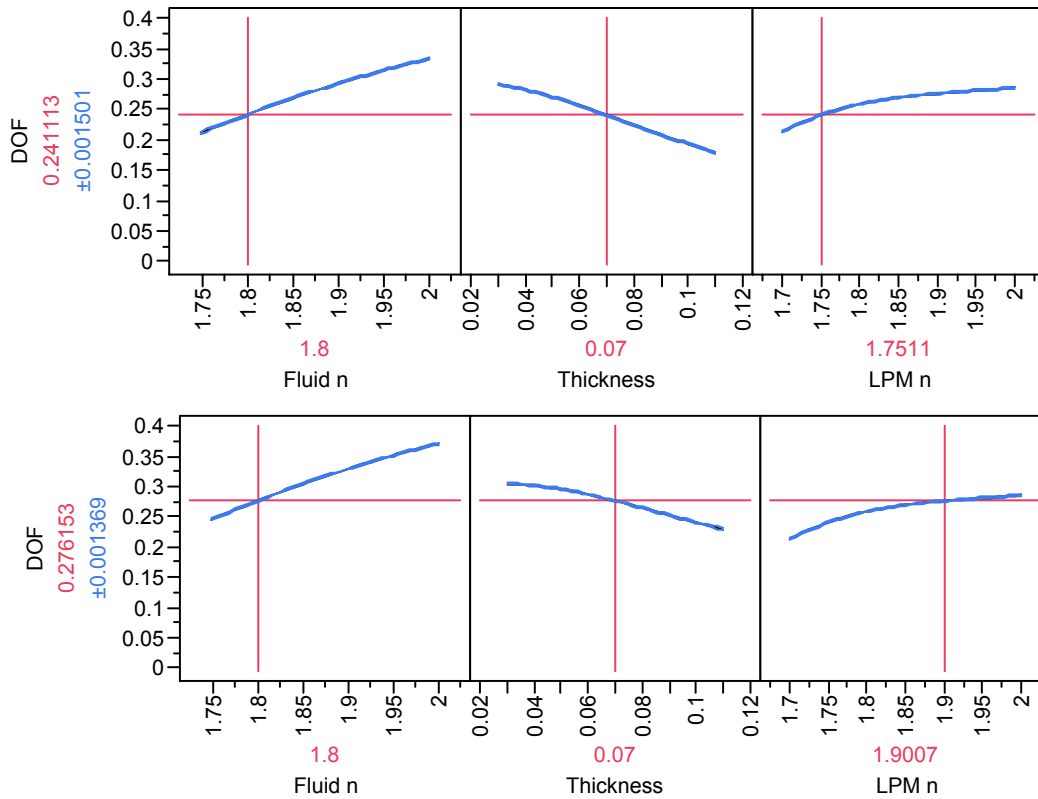

Figure 4 Sensitivity plots generated from PROLITH-simulated data demonstrating the dependence of DOF on immersion fluid index, resist thickness, and resist index. The immersion fluid index demonstrates the greatest potential for process improvement. (ECP)
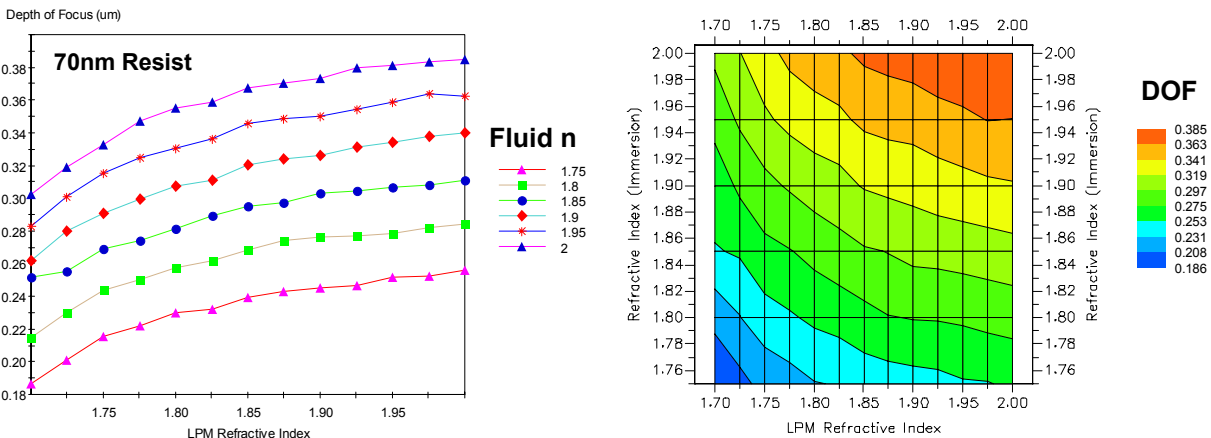

Figure 5A Contour plot of DOF vs. resist RI with various fluid RIs; Figure 5B Contour plot with the RI of the fluid plotted on the y-axis and the resist RI plotted on the x-axis (ECP)

These simulations illustrate the need to increase both the resist and immersion fluid indices to maximize the DOF. It is reasonable to target an index specification of 1.90 for the resist assuming a fluid index of 1.80. As previously mentioned, we must consider the chemistry of such a resist system and the likelihood of obtaining a RI of 1.9. Clearly, modifying a conventional 193 nm resist with a RI of approximately 1.7 and increasing it to 1.9 is not a trivial undertaking.[6]

2. RESULTS AND DISCUSSION

For the past few years, several groups have been working on increasing the RI of 193nm resists.[7-8] Much of the work has focused on the incorporation of heteroatoms into the polymer to increase the polarizability and thus the RI. It appears that the preferred technique to increase the RI of the resist has been through the introduction of sulfur.[7-9] In fact, the options for increasing the resist RI, similar to those for the fluids, 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 193nm resists due to absorbance or photo-induced chemical reactions. So, too, the use of many heteroatoms such as N and P in most forms is prohibited, due to the basic nature of these species when introduced into a resist material. One of the means to introduce a transparent, non-basic nitrogen is through a cyano moiety. Several of these cyano groups could provide transparency and help boost the refractive index. Increasing the structural rigidity of the polymer is also being used. This approach actually works well in concert with the sulfur chemistry as the introduction of sulfur-containing monomers can balance out the increase in T_g caused by more rigid structures. Unfortunately it was determined through significant work by several groups that there are distinct limits to how much sulfur can be incorporated into 193nm type polymers without severely degrading the required resist properties.[6,8-9] The 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 being 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 shown in Figure 6. Different functionalities of sulfur were explored including sulfides, sulfones, thioesters, and thoiethers. This result was also noted by Robert Allen's group at IBM.[10]
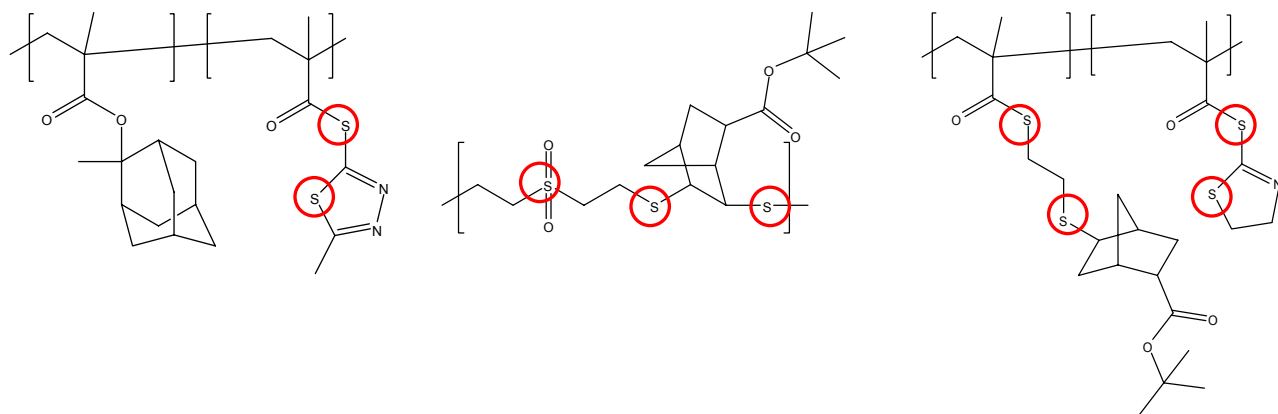

Figure 6 RI and absorbance observed with increasing sulfur (2, 3 and 4 sulfur atoms circled)

Still other groups have taken different and novel approaches to achieve a higher index. For example, IBM used silicon along with carbon in a polymer backbone.[10] These polymers show reasonably good performance; however, the best still showed a RI of just over 1.80.

All these available raises the following question: Is an index of 1.9 really possible? One exercise carried out at SEMATECH was to look at a broad range of lithographic materials. The n and k for lithographic materials from I-line to EUV were surveyed, evaluating whether a 1.9 RI could be obtained for any material at an absorbance of ≤3.0/µm. The process for this exercise was to find the threshold wavelength, λ_{th}, for which the refractive index of the material is maximized with the absorbance below the threshold of 3.0/µm. The value $\lambda-\lambda_{th}$ represents the wavelength difference between the optimal imaging wavelength for this material and the actual wavelength. At a λ-

$\lambda_{th} = 0$, the absorbance for the material evaluated is always 3.0/μm. Figure 7 shows a 248nm/EUV type resist with the RI and absorbance/μm plotted against λ-λ_{th}.

For this material, the λ_{th} value was 236.2nm. The data in this figure at least holds out the possibility for a material that can have both the required RI and absorbance. Table 1 summarizes this relationship for many lithographic materials, indicating there are materials that in principle can meet the stated goals of an RI of 1.9 and absorbance $\leq$ 3.0/μm. The obvious difficulty is designing the chromophores of the organic resist system to have the correct absorbance locations and strength relative to the desired λ_{th} of 193nm.
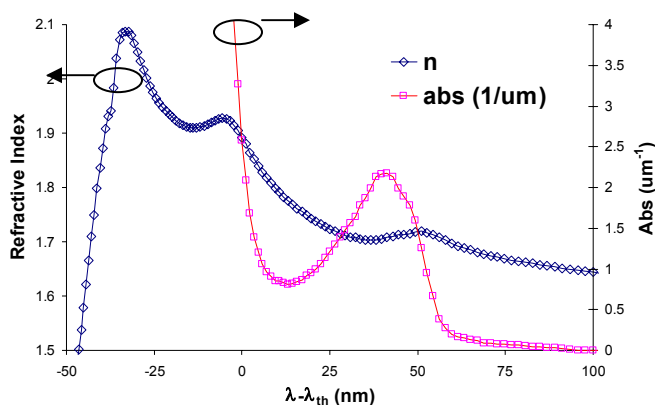

Figure 7 RI and Abs/μm vs. λ-λ_{th} for an 248nm/EUV type resist

Table 2 Survey of available lithographic materials giving the RI at λth and abs =3.0/μm

Material	Class	λth	RI (n_{th})
Brewer AR29a	BARC	220.0	1.751
Shipley AR3	BARC	270.7	1.952
Shipley AR40	BARC	260.0	1.844
AZ LD27	BARC	220.0	1.944
EUV-2D	EUV Resist	236.2	1.904
Sumitomo PAR722	193nm Res.	184.8	1.758
Sumitomo PAR707	193nm Res.	183.2	1.766
Shipley AR19	BARC	224.0	1.763
UT 157nm Res.	157nm Res.	178.4	1.675
Generic SiON	Inorg BARC	344.4	1.978
Shipley UV6	248nm Res.	237.5	1.854
Shipley UV5	248nm Res.	237.5	1.854
Clariant AX100P	193nm Res.	184.8	1.770

The difficulty of increasing the RI while maintaining the desired material properties has been pointed out previously.[6, 11] We can examine the relationship between refractive index and material properties using equation 1, where η is the absolute index of refraction, K_d is the relative permittivity (dielectric constant), and K_m is the relative permeability. It is a good assumption that for all organic species that K_m will be approximately 1 leaving K_d the relative permittivity (dielectric constant) as the only way to dramatically affect the refractive index. Although this relationship is an oversimplification, it describes the situation relatively well for non-polar compounds such as decalin and other similar analogues.

$$\eta = \sqrt{K_d K_m} \qquad \textbf{(Equation 1)}$$

To significantly change the RI, one needs to consider the introduction of a very highly polarizable species that is also nearly transparent at 193nm. Through significant work it has been determined that no easily obtainable organic-based system can be made with the necessary material properties.[12] Given this set of results, our efforts have turned to the investigation of inorganic species. Specifically, the work has focused on nanoparticles that could be transparent at 193nm. Nanoparticles offer the promise of very high index materials. For example, Figure 8 shows the refractive index vs. wavelength for a material that has an index of about 2.90 at 193nm. The result is shown for film thicknesses of 2, 4, and 6 nm. The thickness of these films is consistent with the thickness range of the nanoparticles being investigated. The proof of principle for using nanoparticles in resist has been demonstrated previously.
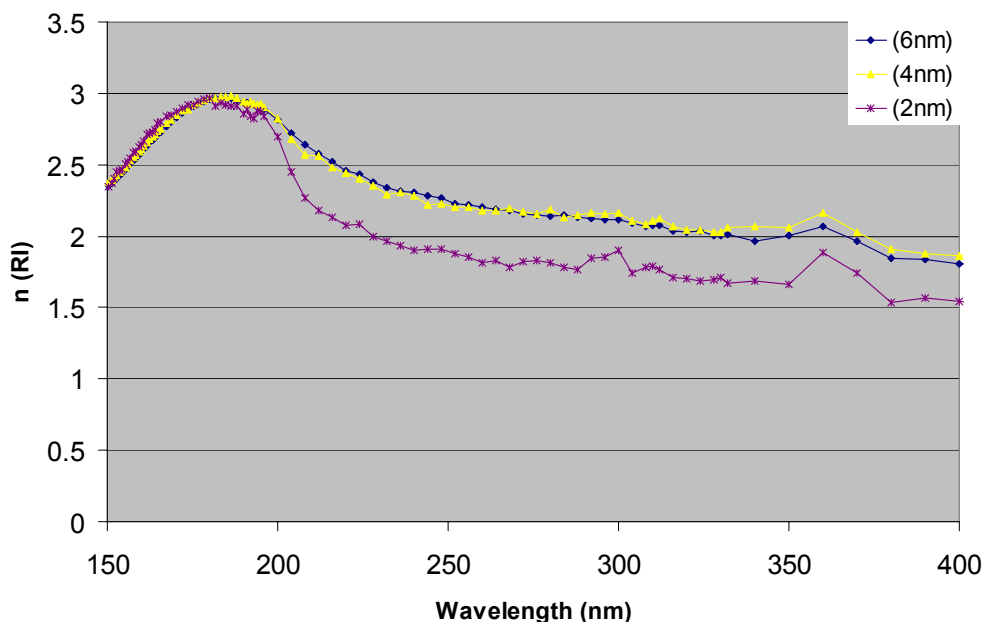

Figure 8 Thin inorganic base films of the target material for nanoparticles

To achieve the required transparency, a small shift in the UV cutoff may be necessary. A shift in the UV cutoff has been shown to be obtainable using a quantum confinement effect.[16] In the case of ZnO, a UV shift of 100nm was observed in reducing the nanoparticle size from 10nm to 2nm.[16] For the material shown in Figure 8, it is expected that only a shift of 10-15nm will be needed to obtain the required transparency. It must be expected that the RI will also shift with the shift in the absorbance; however, because the RI is near the peak of the plateau at 193nm, it is expected that with the UV an RI shift will not dramatically affect the value of the RI of this material. Of course this approach raises several concerns. Top among them will be the possible increase in defectivity on the wafer. Additionally, the impact on standard resist parameters (LER, dissolution rate, etc.) will have to be evaluated with the nanocomposite approach. However, one major advantage of this approach is that no (or very minor) modification will be needed to existing resist platforms. It is clear that the industry does not have the luxury of unlimited time to develop a completely new resist platform with the expectations that it will be used in manufacturing within the next two to three years.

2.1 Nanoparticle Synthesis and characterization

Scheme 1 shows the basic synthetic route for obtaining the bulk of the nanoparticles investigated to date.[17] It has been determined that both reaction conditions and starting material quality are critical to obtain the desired size and shape of nanoparticles. Figure 8 shows a TEM of the optimized nanoparticles with diameters ranging between 2-5nm. If the starting materials are compromised or the reaction conditions are off slightly, rod-shaped nanoparticles are obtained as shown in Figure 8B.

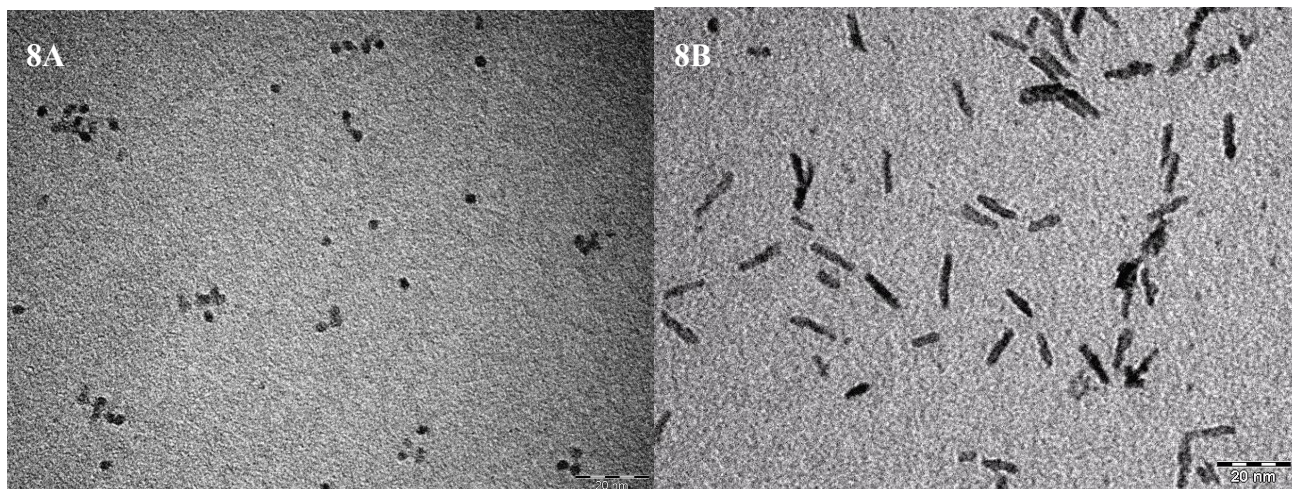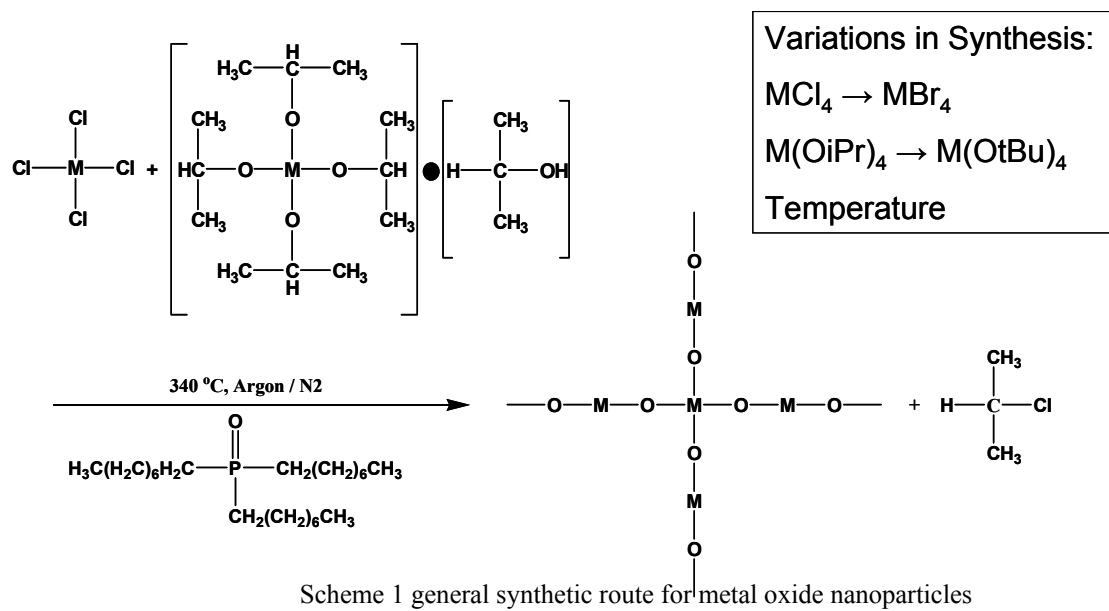Scheme 1 general synthetic route for metal oxide nanoparticles

Figure 8 A) TEM showing optimized metal oxide nanoparticles obtained from the synthetic route shown above 8B) Rod-shaped nanoparticles obtained under conditions that are compromised

In collaboration with IBM, a thin film of these nanoparticles was cast onto a wafer and measured. The results were recently published.[10] The film showed an absorbance of ~ 2.5/μm and a RI ~2.0. It should be noted that these nanoparticles contain some percentage of chlorine, which will raise the absorbance significantly and will probably also dilute the RI somewhat. Work is currently underway to eliminate the contaminating chlorine; however, even at this absorption level, it is clear using these nanoparticles in current resist platforms to increase the RI is a reasonable approach.

A quantity of these nanoparticles was taken and dispersed into resist polymers and examined for roughness. Figure 9 shows a control resist film and a film loaded with 1 wt% nanoparticles, respectively. This minimal loading of nanoparticles causes no increase in roughness. Currently, higher loadings of nanoparticles are being investigated. To homogeneously disperse high loadings (> 10 wt%) of the nanoparticles into the resist, the surface hydroxyls of the nanoparticles may have to be modified. Figure 10 shows one route being explored for a dispersing nanoparticle tether. Another experiment that has been completed is the evaluation of a resist with high (~10%) loading to see if the resist still cleared under 193nm exposure. The resist with the nanoparticles still cleared at a dose consistent with that for the resist without nanoparticles. This result indicates that there was no degradation of the resist system simply by adding the nanoparticles.
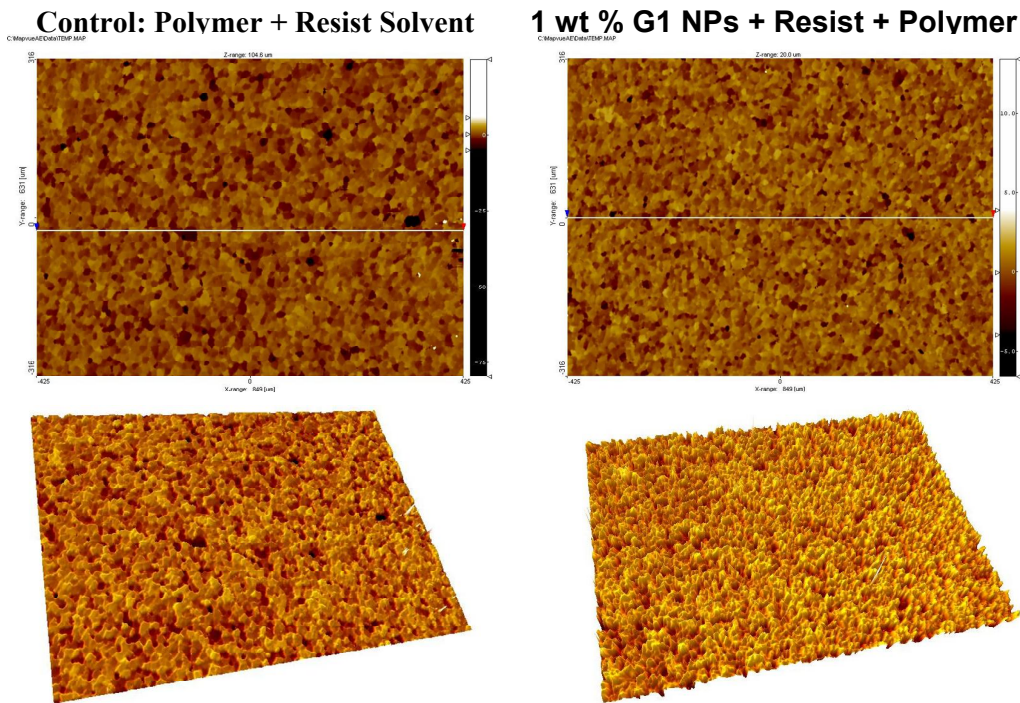
Control: Polymer + Resist Solvent   **1 wt % G1 NPs + Resist + Polymer**

Figure 9 A control resist film and a film loaded with 1 wt% nanoparticles, respectively

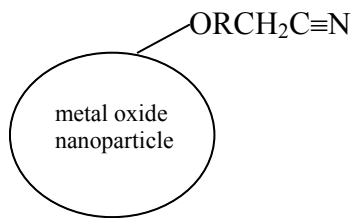

ORCH$_2$C≡N

metal oxide
nanoparticle

Figure 10 Example of a possible tether to a surface hydroxyl used to disperse the nanoparticles

3. CONCLUSIONS

In summary, HIL currently offers a key opportunity to bridge the gap between 45nm and 32nm half-pitch nodes. 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.

All results to date indicate that introducing heteroatoms (i.e., atoms other than C, O, and H) into a resist polymer to raise the RI will not allow an index of ≥1.90 to be achieved. The approach now taken incorporates high index nanoparticles into a conventional resist to achieve the goal. A material has been isolated that even under the current purity has the absorbance necessary to work within existing 193nm resist platforms. The main effort to obtain the required size and quality of the nanoparticles has been achieved and discussed. The path for incorporating high loadings of nanoparticles into 193nm resist systems has been described and is currently under investigation.

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