#828

Journal of Photopolymer Science and Technology
Volume 20, Number 5(2007)643-650©2007TAPJ

Status of High-Index Materials for Generation-Three 193nm Immersion Lithography

[1]Paul A. Zimmerman, [1]Chris van Peski, [1]Bryan Rice, [1]Jeff Byers, [2]Nicholas J. Turro, [2]Xuegong Lei, [2]Juan Lopez Gejo, [3]Vladimir Liberman, [1]Steve Palmacci, [3]Mordy Rothschild, [4]Andrew Whittaker, [4]Idriss Blakey, [4]Lan Chen, [4]Bronwin Dargaville, and [4]Heping Liu

[1]SEMATECH, [2]Columbia University, [3]MIT-LL, [4]University of Queensland
paul.zimmerman@intel.com

Generation-three (Gen-3) immersion lithography can be an enabler for the 32nm half-pitch node. For Gen-3 lithography to be successful, however, there must be three major breakthroughs in materials development: high refractive index ("high-index") lenses, high-index immersion fluids, and high-index photo-resists. Currently a material for a high-index lens element, lutetium aluminum garnet (LuAG), has been identified. However, suitable materials choices remain elusive for both the Gen-3 fluid and resist. This paper reviews the successes and failures in the search for Gen-3 high-index materials.

Keywords: Immersion lithograph, refractive index, resist, lens, fluid

Introduction:

The introduction of water into 193nm lithography allowed its extension beyond the 45nm half-pitch node. The remarkable properties of water made 193 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 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 has to be ≥ 1.8 to achieve a NA approaching 1.7 and thereby enabling imaging at the 32nm node.[5] The challenges of developing these materials as well as the status of each material will be discussed in subsequent sections.

High-Index Lens Materials:

The drive to immersion lithography comes from the need to increase the numerical aperture of exposure lenses. Increasing the index of the medium between the lens and wafer is only part of the requirement. It is also necessary to increase the index of the resist fluid and the last lens element.

The prime requirements for the last element material are high index of refraction (>1.8), low absorbance at 193nm (<0.01), and low intrinsic birefringence (<10nm/cm). Absorbance and index are coupled together, as wavelength approaches the band edge of the material, index and absorbance both increase. The task is to find a material with a band edge far enough below 193nm to allow adequate transmission but close enough to provide a high index of refraction. The material must have low intrinsic birefringence and a high damage threshold at 193nm, as well as meet the commercial requirements of manufacturability, cost, and ESH considerations.

A number of candidates have been identified. Spinel, $MgAl_2O_4$, has an index close to 2, but it also has an intrinsic birefringence of 52nm/cm,[6] which is significantly higher than the 10nm/cm target. The ceramic form of spinel is attractive because birefringence is cancelled by the random grain orientation of the ceramic. Spinel is currently manufactured for use as

transparent armor, but material tested to date has not met absorbance and scatter requirements.[6]

An exhaustive search of the periodic table has identified garnets as a likely class of materials. Two classes of garnets exist: natural garnets following $X_3Y_2Z_3O_{12}$ and synthetic garnets following $X_3Y_5O_{12}$. Of all the natural garnets, the silicate and germanate garnets hold the greatest promise. Silicate garnets are abundant in nature, but they are difficult to grow in the laboratory because of the high pressure and temperature required. Pyrope, $Mg_3Al_2Si_3O_{12}$, has been grown in the laboratory, but samples grown to date have been limited to a few mm in size, and scale-up is not within the current state-of-the-art. Germanate garnets, in contrast, can be grown using traditional crystal growth techniques (i.e., Czochralski), but unfortunately have been found to have absorption edges no shorter than 225nm.[7]

That leaves the synthetic garnets, which have been extensively investigated. The most promising candidate is lutetium-aluminum garnet (LuAG), $Lu_3Al_5O_{12}$, which has an index of 2.14[8] and intrinsic birefringence of 30.[7] The intrinsic birefringence is greater than desired, but the lens manufacturers have developed ways of compensating for this birefringence in the lens design. LuAG has been grown commercially, and although the production specifications needed for the last lens element have not yet been achieved, good progress has been made.[9] The issues to be solved are absorbance, stress birefringence, and size. Absorbance is driven by trace impurities. Development efforts are underway to purify the raw materials and to address stress birefringence. Scaling up to larger sizes is also under development.

Generation -3 Fluids:

Unlike the lens material, no Gen-3 fluid has yet been identified. In many ways, the development of fluid is the most daunting task for the materials. This is because of the requirements on the fluid at 193nm, including a refractive index ≥ 1.8; an absorbance < 0.25/cm; < 300 ppm dn/dT; and a viscosity <50 cps. If we initially focus on absorbance$_{(193)}$ and RI, we can immediately eliminate most chemical species from consideration as an HIL fluid. For example, organic halides (of which Cl, Br, and I would help to give a significant increase in the RI) compared to non-halide containing organics are all reactive at 193nm. Alcohols and ethers are too reactive under 193nm exposure; ketones and aldehydes are absorbing and reactive. Recently highly transparent organic fluids were exposed to 193nm as described earlier.[10] These fluids had a base absorbance of 0.03/cm, but in each case the transparency of the fluids degraded rapidly as shown in Fig. 1.

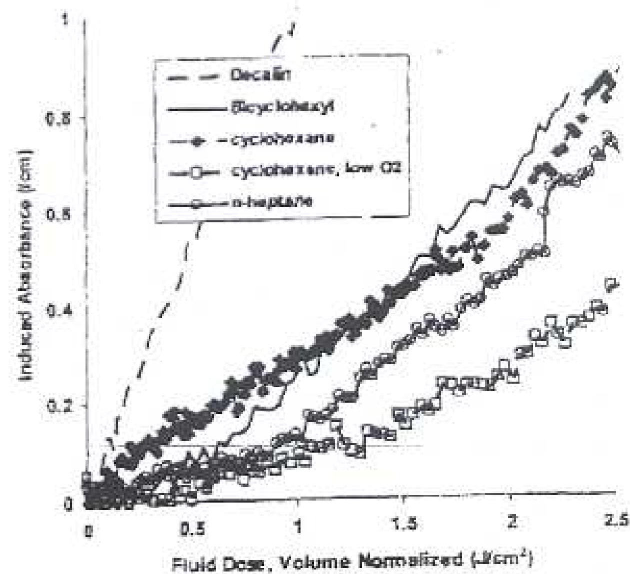

Fig. 1. A comparison of organic fluids that are degraded over time during exposure

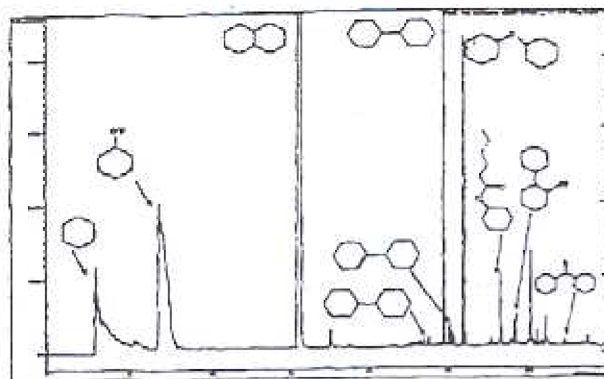

Fig. 2 GC-MS of exposed cyclohexane. Note that the detector is off for the first three minutes so that it is not overwhelmed

Fig. 2 shows a gas chromatography mass spectroscopy (GC-MS) from a sample of exposed cyclohexane. Remember that this was a material that had a starting absorbance of ox0.03/cm. Degradation products containing ygen are probably the result of residual oxygen in the and are probably formed through degradation of system a hydroperoxy intermediate.

Other species not containing oxygen are formed through termination of radical species. This degradation was consistently observed for other organics, indicating that this it is a fundamental process that cannot be eliminated. Several prospective Gen-2 fluid suppliers have implemented an in-line purification system, no doubt to eliminate the inevitable degradation products.[11, 12] Using this in-line purification and recycling system, the Gen-2 fluids are now suitable for use with a reasonable lifetime. However, still in question is whether the lens lifetime will be satisfactory with the use of Gen-2 fluids. There is great concern from current results[10] indicating that cleaning will be required after relatively short (1-2 days) intervals.

To develop Gen-3 fluids, we first consider a pure organic system containing only C and H. This approach allows the choice of possible materials to be rapidly narrowed. Fig. 3 shows the relationship between refractive index n(d) and density for various hydrocarbon species. This trend has been shown by others previously.[13] Examining the graph, it rapidly becomes clear that increasing the number of rings increases the RI significantly. Unfortunately, structures like adamantane or diadamantane are solids and thus provide no utility for this application. Following the density relationship to its inevitable conclusion of the most dense C_xH_y organic leads to C_8H_8, cubane. This too is a solid at room temperature; however, a derivative, methylcubane (MC), is a liquid at room temperature. The expected density of MC is ~ $1.2 g/cm^3$, which should translate into an RI of ≥1.8 at 193nm. This material is currently being evaluated by SEMATECH as a Gen-3 fluid, and results are forthcoming. In addition to materials containing only carbon and hydrogen, materials containing heteroatoms are also being examined.

To avoid the fluid degradation inherent in organic systems, a different approach is being evaluated. This approach uses a nanocomposite to obtain the high-index required. The nanocomposite is made up of an inorganic core with an RI ≥ 2.4 at 193nm. In an aqueous solution at a 50wt% loading, this would give an RI of about 1.86. In an organic solution, possibly a Gen-2 type fluid, approximately a 30wt% loading would be required. The complexity of this solution cannot be overstated. First, it will be required to have nanoparticles with diameters of ≤5nm to prevent scattering and realize some benefit from the quantum confinement effect.[14] If required, a dispersing agent will be attached. This agent will be attached to only as many sites as are needed to achieve dispersion. This chemistry will have to be carefully controlled. An example of how an ideal dispersion agent may look is shown in Fig. 4. A cyano group is chosen because of the favorable interaction with water or an organic solution with only one methylene group being used between the cyano group and the tethering heteroatom. As was discussed earlier, the fewer carbon centers used, the better to reduce any potential photochemistry.

Three approaches are being pursued to develop a Gen-3 fluid, but the goal remains high

risk as a base system must be identified before the end of 2007 to meet the timeline for the 32nm half-pitch node.

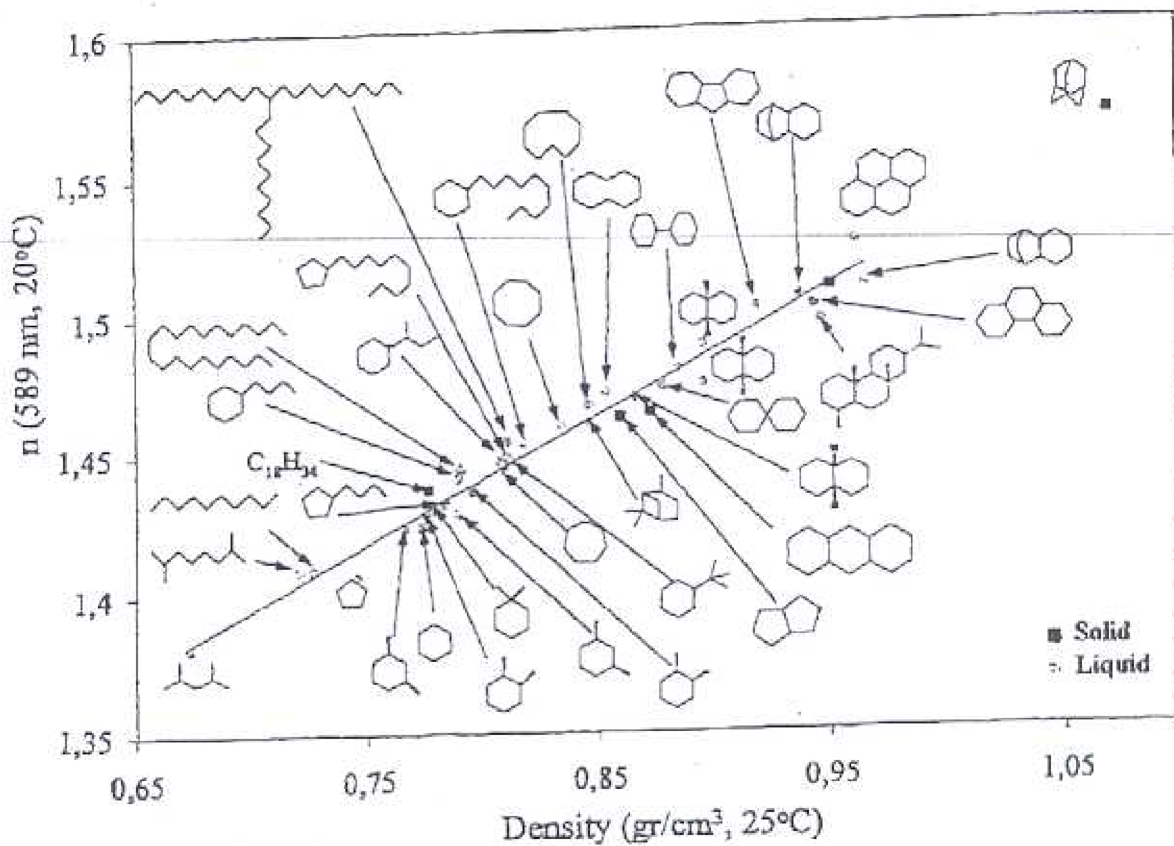

Fig. 3 Plot of RI vs. density for non-hereroatom containing hydrocarbons showing the distinctive trend

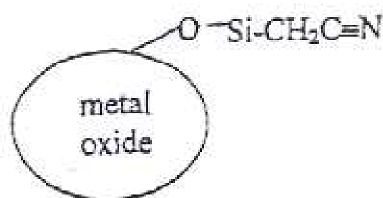

Fig. 4 Example of a possible tether to be used to disperse a nanoparticle

Generation-3 Resist:

A final but no less important piece of the puzzle for HIL is the resist. The refractive index goal for a Gen-3 resist is 1.9.[2,4,5] Currently, only two research groups are openly working on the development of a high-index resist.[15,16] It appears that the preferred technique to increase the RI of the resist is through the introduction of sulfur. 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 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 have the impact of balancing out the increase in T_g caused by more rigid structures.

I s 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, □$_{th}$, for which the refractive index of the material is maximized with the absorbance below the threshold of 3.0/□m. The value λ-λ_{th} represents the wavelength difference between the optimal imaging wavelength for this material and the actual wavelength. At a λ-λ_{th} = 0, the absorbance for the material evaluated is always 3.0/μm. Fig. 5 shows a 248nm/EUV type resist with the RI and absorbance/μm plotted against λ-λ_{th}.

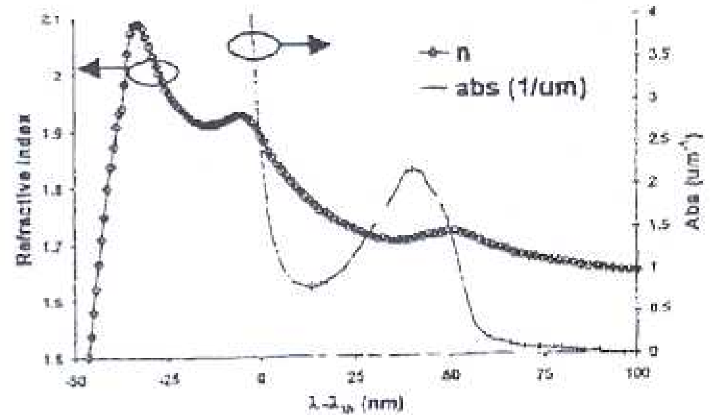

Fig. 5 RI and Abs/μm vs. λ-λ_{th} for an 248nm/EUV type resist.

For this material, the λ_{th} value was 236.2nm. The data presented 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 that there are materials in principle that can meet the stated goals of an RI of 1.9 and absorbance ≤ 3.0/μm.

Table 1 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
AZ1.D27	BARC	220.0	1.944
EUV-2D	EUV Resist	236.2	1.904
Sumitomo PAR722	193nm Res.t	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
Clarriant AX100P	193nm Res.	184.8	1.770

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_{ch} of 193nm.

Currently, the highest index polymer that has been imaged at 193nm gives a refractive index of 1.805 (see Fig. 6). Unfortunately, the absorbance for this species is much higher (~7.5/μm) than the ~3.0/μm that will be required for imaging 90nm of resist.

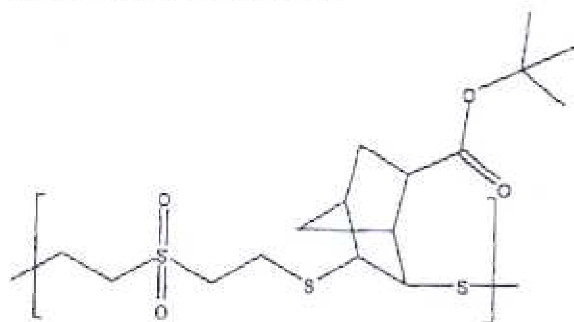

Fig. 6. Polymer that has been imaged at 193nm showing an RI >1.8

Initial observations indicate that as the number of sulfur atoms in repeat units is increased, there is a concurrent increase in absorbance. This trend is shown in Fig. 7. Fig. 8 compares the calculated spectra for molecules with differently bonded S species.

This result shows that there seems to be a fundamental limitation on the amount of sulfur that can be introduced into a polymer. The result demonstrates that quickly obtaining a resist with an RI >1.8 through this approach is not possible. It appears that to stay within the absorbance budget, it is not possible to have more than 20-25 wt% S in the polymer. A slight increase in sulfur may still be possible by using all thioethers, which absorb less than sulfones or thioesters.

Beyond sulfur, two major approaches are being investigated. The first approach is to increase the rigidity of the sulfur-containing polymer as a means to drive the RI higher, for example with a diadamantane chemistry.[17]

The second approach beyond sulfur incorporation is to add an inorganic nanocomposite with a high RI (>2.4 at 193nm). If we can obtain a polymer with a base RI of approximately 1.8 at 193nm then the loading of a nanocomposite needed to reach a RI of 1.9 will be modest, making such a system possible. However, this approach will raise 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.

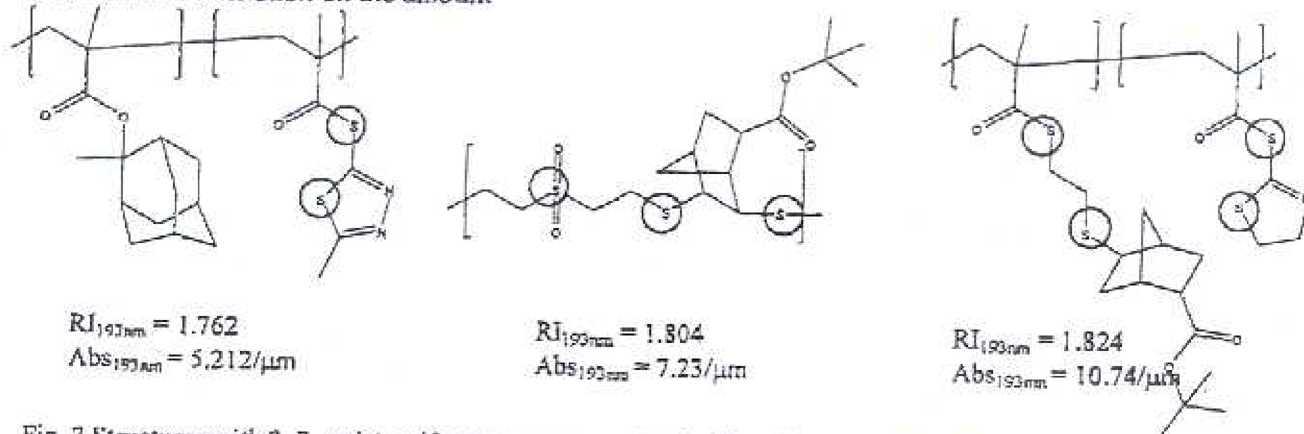

Fig. 7 Structures with 2, 3, and 4, sulfur atoms per repeat unit (the sulfur atoms are circled)

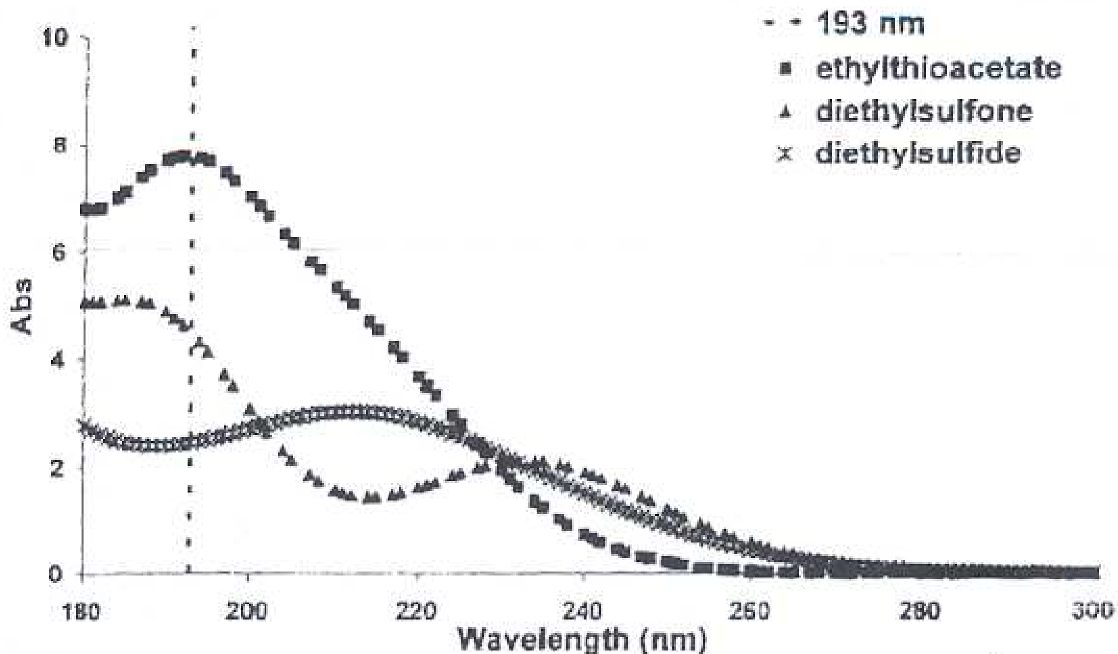

Fig. 8 Comparison off calculated absorbance verses wavelength for thioethers, thioesters, and sulfones

Conclusions

In summary, HIL currently offers a key opportunity to bridge the gap between 45nm and 32nm half-pitch nodes. Although there are several daunting material challenges, no fundamental showstoppers are apparent. It should be noted that the current 193nm resists have been modified and optimized for over a decade to achieve the high imaging performance that is now routine. Clearly, much work and some breakthrough chemistry is needed to achieve the goal of high-index resists and fluids suitable for Gen-3 immersion lithography.

Disclaimers:

SEMATECH: Advanced Materials Research Center, AMRC, International SEMATECH Manufacturing Initiative, and ISMI are servicemarks of SEMATECH, Inc. SEMATECH, the SEMATECH logo, Advanced Technology Development Facility, ATDF, and the ATDF logo are registered servicemarks of SEMATECH, Inc. All other servicemarks and trademarks are the property of their respective owners

649

References:

1) R.H. French, V. Liberman, H.V. Tran, J. Feldman., D.J. Adelman, R.C. Wheland, W. Qiu, S.J. McLain, O. Nagao, M. Kaku, M. Mocella, M.K. Yang, M.F. Lemon, L. Brubaker, A.L. Shoe, B. Fones, B.E. Fischel l, K. Krohn, D. Hardy, C.Y. Chen, "High Index Immersion Lithography with 2nd Generation Immersion Fluids To Enable Numerical Apertures of 1.55 For Cost Effective 32 nm Half Pitches," Proc. SPIE Opt. Microlitho., In Press (2007).

2) S. Kusumoto, M. Shima, Y. Wang, T. Shimokawa, H. Sato, K. Hieda, "Advanced materials for 193 nm immersion lithography," Poly. Adv. Tech., Volume 17, Issue 2 , 122 – 130, (2006).

3) B.W. Smith, J. Zhou, F. Fan, A. Bourov, "Inorganic immersion fluids for ultrahigh numerical aperture 193 nm lithography," Applied Optics, Vol. 45, Issue 13, pp. 3077-3082, (2006).

4) W. Conley, S. Warrick, C. Garza, P-J Goirand. J.-W Gemmink, D.Van Steenwinckel, "Application of Beyond Water Immersion to Device level Imaging," 3rd Intl. Symp. on Immersion Lithography, Kyoto, Japan, Oct 2006.

5) B.W. Smith, J. Zhou, "Snell or Fresnel – The influence of material index on hyper NA

lithography,"Proc. SPIE Optical Microlithography, In Press (2007)
6) J. H. Burnett, S.G. Kaplan, E.L. Shirley, D. Horowitz, W. Clauss, A. Grenville, and C. Van Peski , "High-index optical materials for 193nm immersion lithography," Proc. SPIE 6154, 615418 (2006)
7) J. H. Burnett, S.G. Kaplan, E.L. Shirley, D. Horowitz, D. Josell, W. Clauss, A. Grenville, C. Van Peski, "SEMATECH H-I Materials for 193nm Immersion Lithography," H-I Materials Crit. Rev. October 2, 2006, Kyoto
8) L. Parthier, G. Wehrhan, D. Keutel, K. Knapp, "Development of optical material LuAG for hyper NA Immersion Lithography," SEMATECH High Index Materials Critical Review October 2, 2006, Kyoto
9) L. Parthier, G. Wehrhan, D. Keutel, K. Knapp, Development status of high-index lens material LuAG for ArF hyper-NA immersion systems, Proc. SPIE Optical Microlithography, [6520-58] (2007)
10)V. Liberman, M. Rothschild, S.T. Palmacci, P.A. Zimmerman, A. Grenville, Laser Durability Studies of High Index Immersion Fluids: Fluid Degradation and Optics Contamination Effects, Proc. SPIE, In Press (2007)
11) R.H. French, W. Qiu, M.K. Yang, R.C. Wheland, M.F. Lemon, A. L. Shoe, D.J. Adelman, M.K. Crawford, H.V. Tran, J. Feldman, S.J. McLain, S. Peng, Second Generation Immersion Fluids for 193nm Immersion Lithography, Proc. SPIE Optical Microlithography, (2006)
12) K. Kawaguchi, T. Kishida, T. Furukawa, T. Miyamatsu, T. Tominaga, M. Slezak*, Y. Wang, K. Yamada, K. Hieda, Third-Generation Fluid for Generation Fluid for ArF Immersion Lithography, 3rd Intl. Symp. on Immersion Lithography, Kyoto, Japan, Oct 2006.
13) P.A. Hiltner, Y.S. Papir, I.M. Krieger, (1881). Diffraction of light by nonaqueous ordered suspensions. J. Phys. Chem., 1971-75.
14) C. Li, S. Xiyu, W. Zhenyu, Z. Bingsuo, D. Jiahua, X. Sishen, Quantum confinement effect of ZnO nano-particles, Chemical Journal on Internet, Vol.4 No.9 p.45, 2002.
15) Y. Nishimura, T.Kawakami, K. Hoshiko, T. Tominaga, M. Shima, S. Kusumoto, T. Shimokawa, K. Hieda, "Novel photoresist materials development with high refractive index at 193nm for next generation immersion lithography." 3rd Intl. Symp. on Immersion Lithography, Kyoto, Japan, Oct 2006.
16) I. Blakey, L. Chen, B. Dargaville, H. Liu, D. Hill, G. A. George, Rasoul F., Whittaker A.K., Conley W.E., Rice B., Zimmerman P., "Strategies for the Generation of High Refractive Index Polymers for 193 nm Immersion Photoresist Formulations," 3rd Intl. Symp. on Immersion Lithography, Kyoto, Japan, Oct 2006.
17) R.R. Dammel, M. Padmanaban, S. Chakrapani, D. Parthasarathy, G. Lin, D. Rahman, D. McKenzie, "Highly Dry Etch Resistant 193 nm Photoresists Based on Diamantane Chemistry," 3rd Intl. Symp. on Immersion Lithography, Kyoto, Japan, Oct 2006.