High Index Aqueous Immersion Fluids for 193nm and 248nm Lithography

B. W. Smith, Y. Fan, J. Zhou, A. Bourov, L. Zavyalova, E. Piscani, J. Park, D. Summers, F. Cropanese

Rochester Institute of Technology
Center for Nanolithography Research

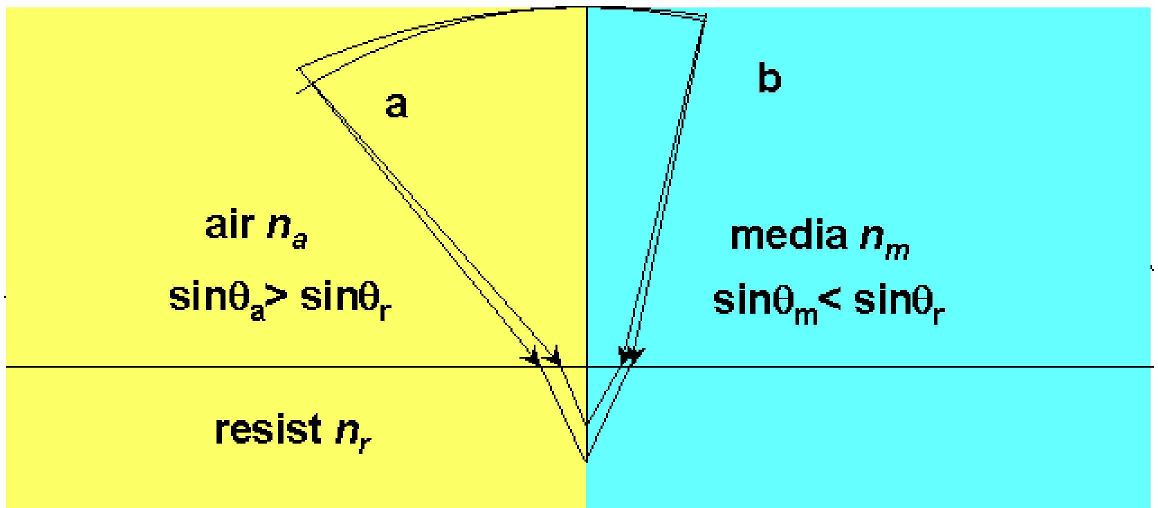
193nm Immersion Lithography for sub-45nm nodes

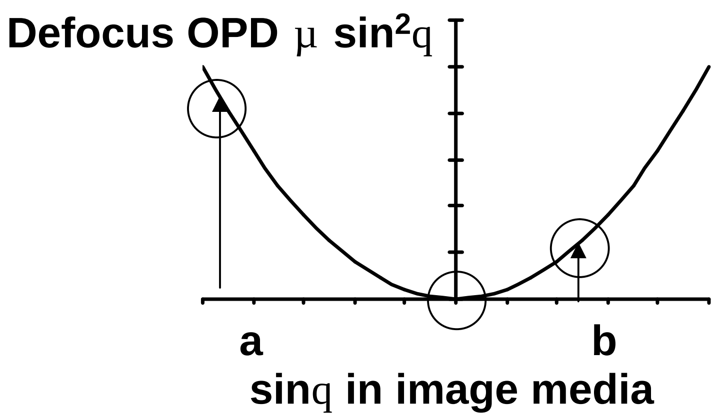
- Sub-45nm 193i and sub-65nm 248i requires high index fluid development
- The 45nm node corresponds to a 0.33k1 at 1.44 NA (the index of water).
- A half-pitch of 38nm corresponds to a 0.28k1 at 1.44.
- Sub-45nm is not likely with water alone.
- Increasing the refractive index of the immersion fluid is desirable.

Homogeneous Immersion

Increasing refractive indices – the defocus effect

Low index (air) imaging **High index imaging**





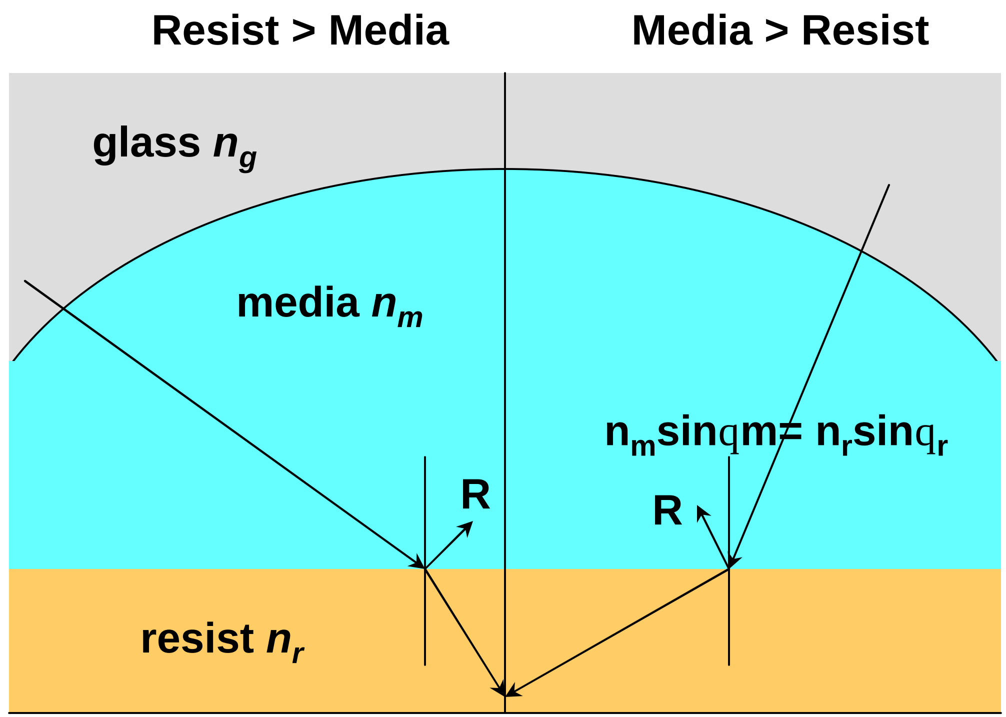
The defocus wave aberration is proportional to sin^{2}q

Higher indices reduce defocus OPD at equivalent NA values

A small (NA/n) is desirable - achieved with high media index

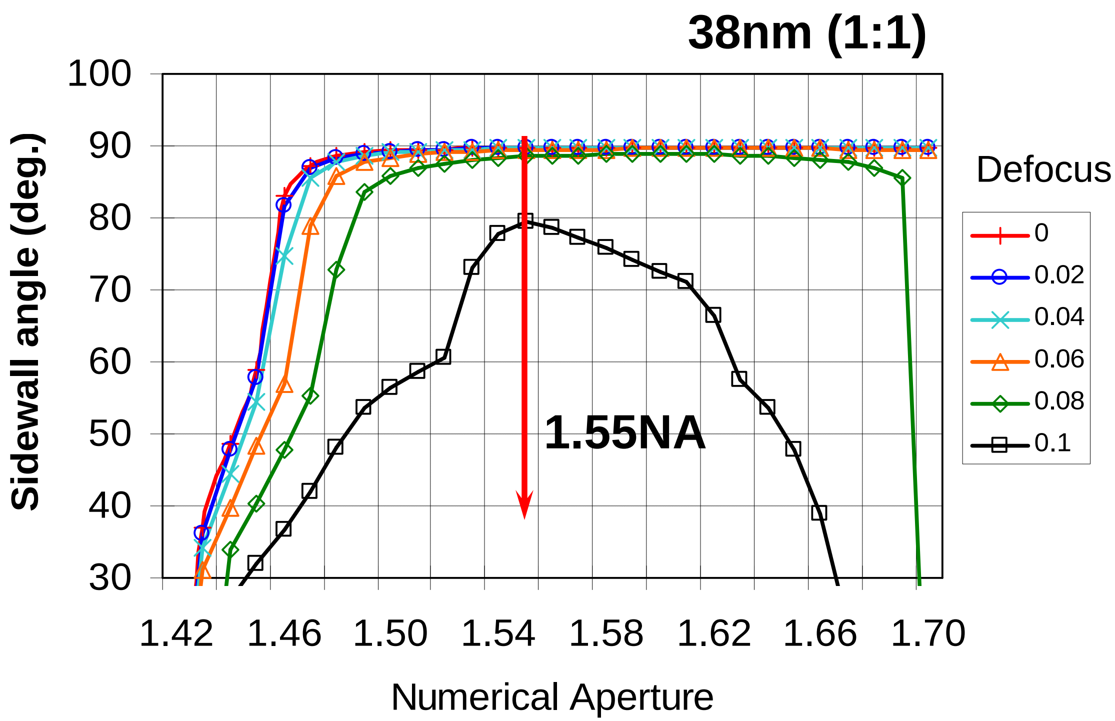
Homogeneous Immersion

Increasing refractive indices – the refractive effect



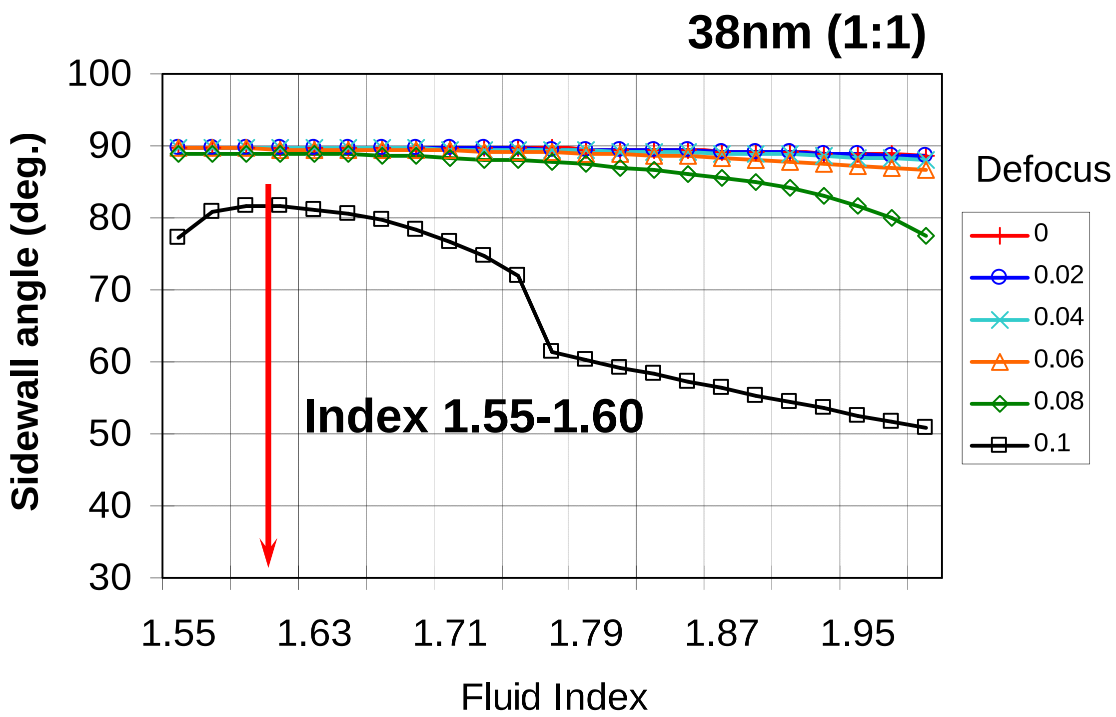
- The glass index is not a concern unless surface is planar
- The maximum NA is limited to min[n_m,n_r]
- Reflectivity is determined by index disparity
- Index matching is desirable - fluid index should be close to resist index

193nm Immersion for sub-45nm
NA Requirements



- Resist simulations of 38nm (1:1) in a 70nm resist LPM
- TE polarization and alternating PSM
- Sidewall angle used as metric vs. defocus
- Target NA is 1.55 - not possible with water

193nm Immersion for sub-45nm
Fluid Index Requirements



- NA held at 1.55
- Fluid index varied from 1.55 to 2.0
- Target fluid index is 1.55-1.60

Increasing Water Index in the UV

Inorganic approach

- UV-vis absorption involves excitation of e^- from ground
- Solvents provide "charge-transfer-to-solvent" transitions (CTTS)
- CTTS and l_{max} for halide ions is well documented [1]

$$F^- < (OH)^- < Cl^- < Br^- < I^-$$

- Alkalai metal cations can shift l_{max} lower [2]

$$Cs^+ < Rb^+ < K^+ < Li^+ < Na^+ < NH_4^+ < H_3^+O$$

- d l_{max}/dT is positive (~500ppm/°C), d l_{max}/dP is negative
- Goal to approach "anomolous dispersion" with low absorbance

[1] E. Rabinowitch, Rev. Mod. Phys., 14, 112 (1942)

[2] G. Stein and A. Treinen, Trans. Faraday Soc. 56, 1393 (1960)

Effect of Anion on Absorption of Water

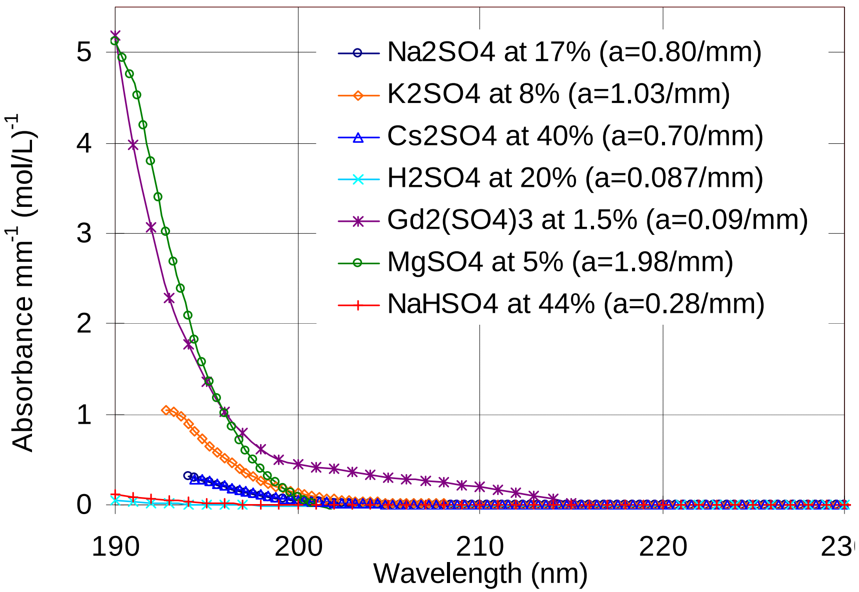
Anion in water	Absorption Peak [3]	
I^-	5.48eV	227nm
Br^-	6.26	198
Cl^-	*6.78*	*183*
ClO_4^{-1}	6.88	180
HPO_4^{2-1}	*6.95*	*179*
SO_4^{2-1}	*7.09*	*175*
$H_2PO_4^-$	*7.31*	*170*
HSO_4^-	*7.44*	*167*

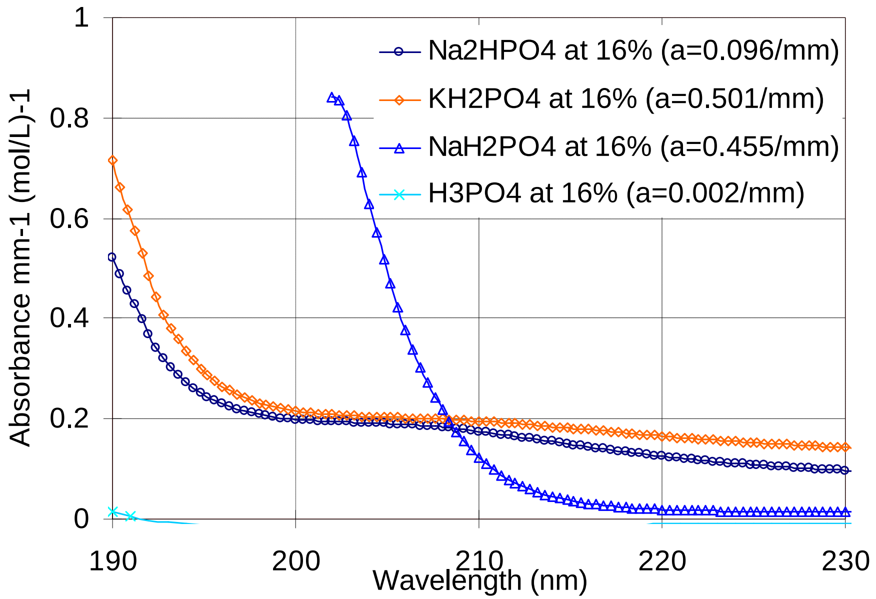
Halogens Potential 248nm candidates

Phosphates and Sulfates Potential 193nm/248nm candidates

[3] Various sources including M.J. Blandamer and M.F. Fox, <u>Theory and Applications of Charge-Transfer-To-Solvent Spectra</u>, (1968).

Measured UV Absorbance Spectra of Sulfates and Phosphates in Water





- **Solutions normalized to mole concentration of cation**
- **Fluids with absorbance < 0.1/mm become interesting**
- **Several candidates for 248nm, fewer for 193nm**
- **Impurities in research grade material may contribute**

Fluid Absorbance at 193nm and 248nm

Fluids	a(mm^{-1},@193nm)	a(mm^{-1},@248nm)
$CaCl_2$@20%	-	0.0257
CsCl@20%	-	0.0022
CsI@20%	-	-
KCl@20%	-	0.0031
$ZnBr_2$@20%	-	0.0129
Na_2SO_4@17%	1.144	0.0014
K_2SO_4@8%	1.03	6.00E-4
Cs_2SO_4@40%	0.706	0.0017
$Gd_2(SO_4)_3$@1.5%	0.0085	0
$MgSO_4$@5%	1.05	0
NaH_2PO_4@16%	0.429	0.110
Na_2HPO_4@16%	4.72	0.0154
KH_2PO_4@16%	0.571	0.163
H_3PO_4@20%	0.0251	0.00213
H_2SO_4@20%	0.246	0.00183
HCl@20%	2.91	0.0015

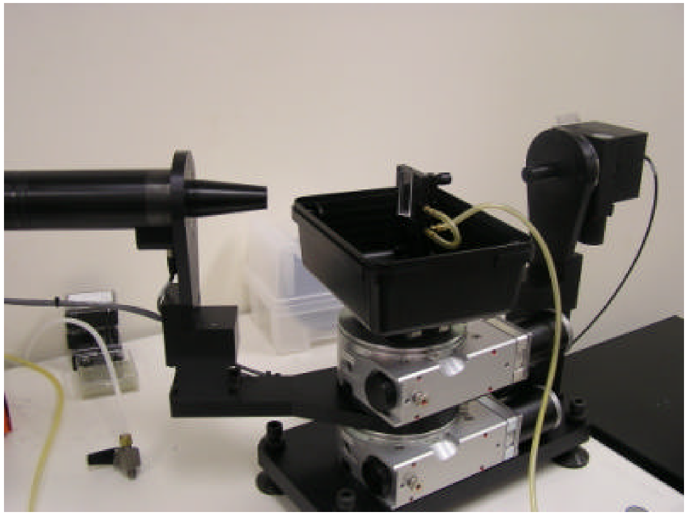
*Data obtained by fit of absorption peak

Index Measurement of Fluids

Screening of Inorganic Candidates

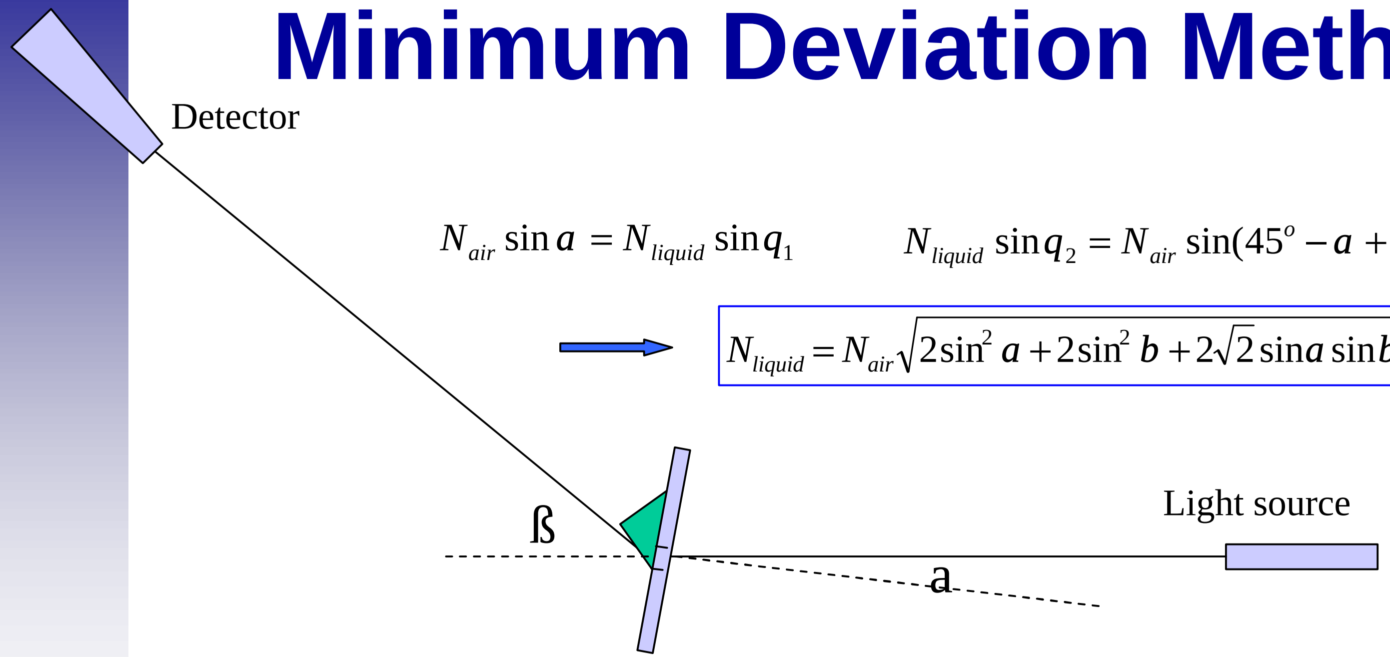
- Fluid index and dispersion measurement needed for screening
- Measurement to $1x10^{-3}$ is adequate for initial work
- Minimum Deviation Method is accurate to < $1x10^{-4}$
- WVASE tool provides an accurate goniometer and detector

Fluid prism cell



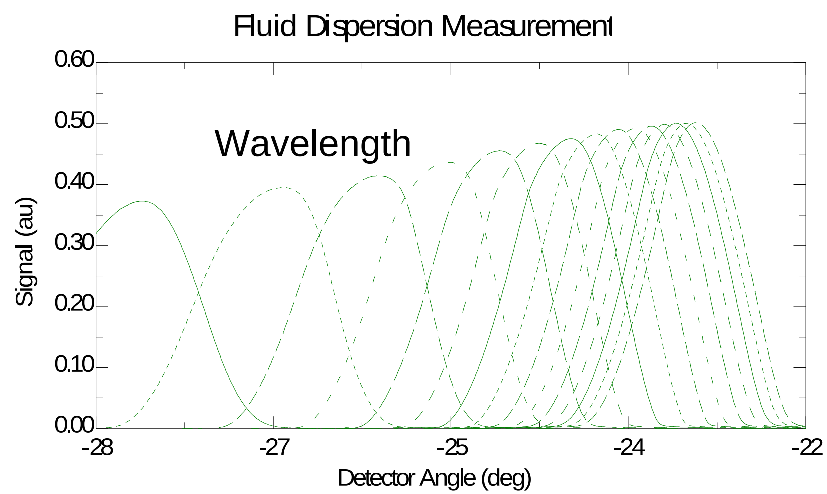
Modified Woollam tool for fluid index

Minimum Deviation Method



$$N_{air} \sin\alpha = N_{liquid} \sin\theta_1 \qquad N_{liquid} \sin\theta_2 = N_{air} \sin(45^o - \alpha + \beta) \qquad \theta_1 + \theta_2 = 45^o$$

$$\Rightarrow \boxed{N_{liquid} = N_{air}\sqrt{2\sin^2\alpha + 2\sin^2\beta + 2\sqrt{2}\sin\alpha\sin\beta}}$$



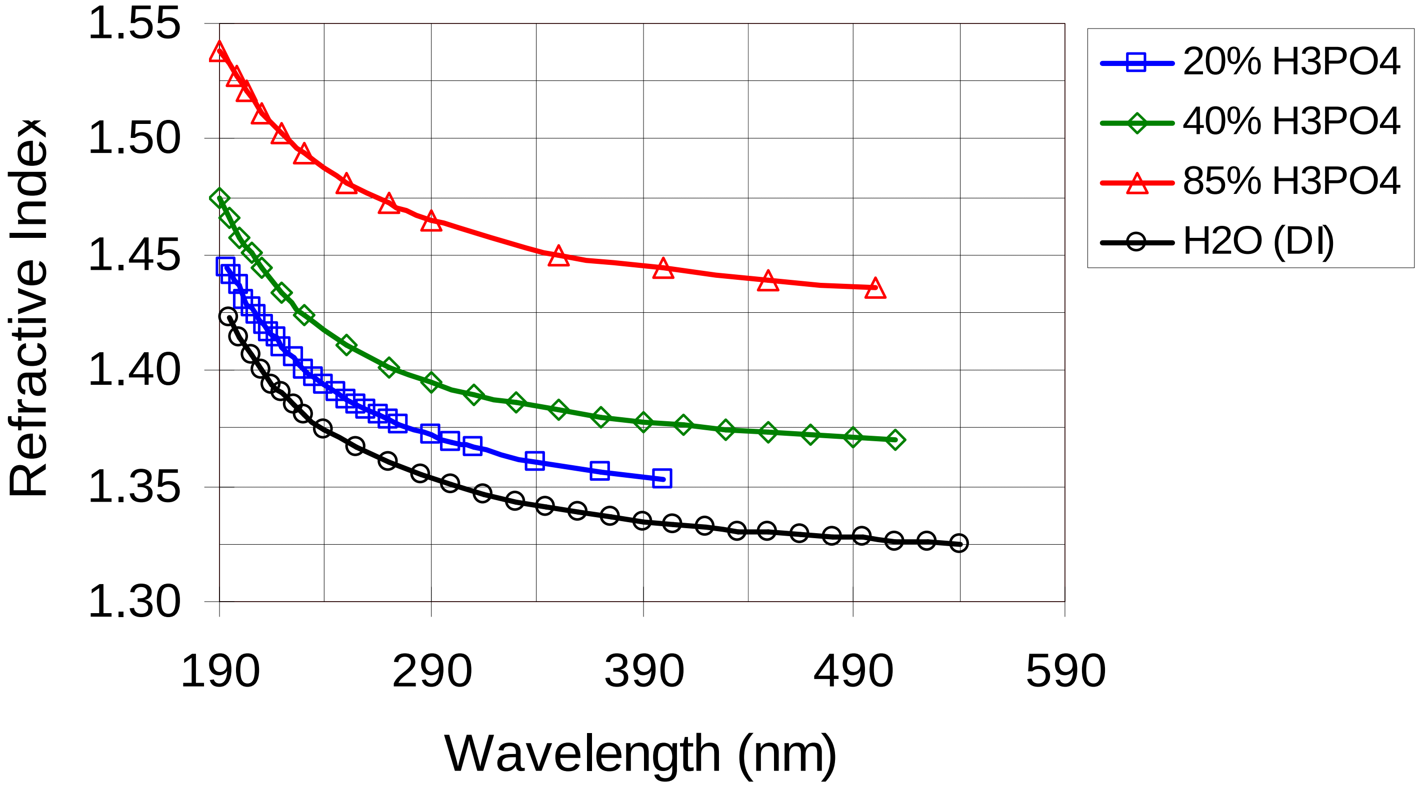
Fluid Refractive Index and Dispersion

Fluids	Refractive index @ 193nm	Refractive index @ 248nm	Cauchy parameters A	Cauchy parameters B	Cauchy parameters C
HCl@37%	1.583	1.487	1.3997	0.0032	0.000134
CsCl@60%	1.561	1.466	1.3912	0.0020	0.000160
H_2SO_4@20%	1.472	1.418	1.3635	0.0022	0.000068
H_2SO_4@96%	1.516	1.469	1.4151	0.0027	0.000040
$NaHSO_4$@44%	1.473	1.418	1.3643	0.0021	0.000074
Cs_2SO_4@40%	1.481	1.422	1.3685	0.0020	0.000083
Na_2SO_4@30%	1.479	1.423	1.3667	0.0023	0.000069
H_3PO_4@20%	1.452	1.398	1.3486	0.0018	0.000077
H_3PO_4@40%	1.475	1.420	1.3723	0.0015	0.000085
H_3PO_4@85%	1.538	1.488	1.4316	0.0028	0.000042
H_2O (DI)	1.435	1.373	1.3283	0.0021	0.000067

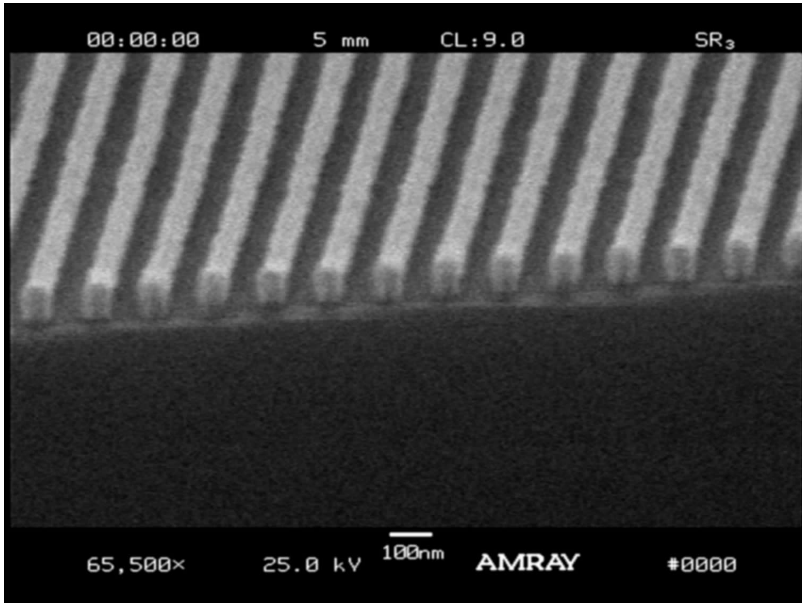
Hydrogen Phosphates

*Data obtained by Cauchy model fit are labeled red. Experimental data are not available due to high absorption

Refractive Index of Hydrogen Phosphates



Imaging in 85% Hydrogen Phosphate
Fluid Refractive Index 1.54



68nm imaging
TE polarization

- **193nm resist (100nm Shipley 1020B) imaged with no top-coat**
- **No measured thickness loss or surface effects**
- **Surface contamination effects are reduced compared to water**
- **No contamination at optics interface**
- **Initial results are encouraging**

Summary

- Sub-45nm 193i and sub-65nm 248i requires high index fluid development
- A minimum deviation method has been developed for fluid index screening
- Immerison fluid index has been increased to 1.54 (193nm) and 1.49 (248nm) using halides, phosphates, and sulfates

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