High Refractive Index Liquid for 193nm Immersion Lithography

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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 λ_{max} for halide ions is well documented** [1]

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

- **Alkalai metal cations can shift λ_{max} higher** [2]

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

- **The goal is to approach absorption edge of a fluid**

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

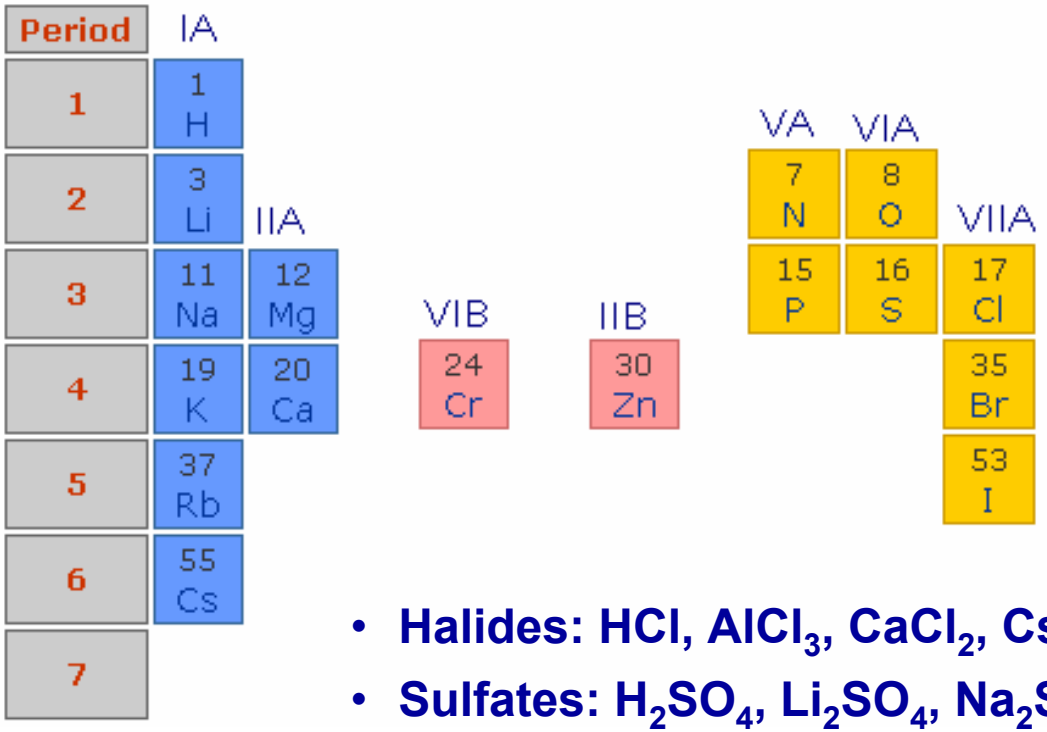
[2] G. Stein and A. Treinen, Trans. Faraday Soc. 56, 1393 (1960)

Effect of Anion on Absorption of Water

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

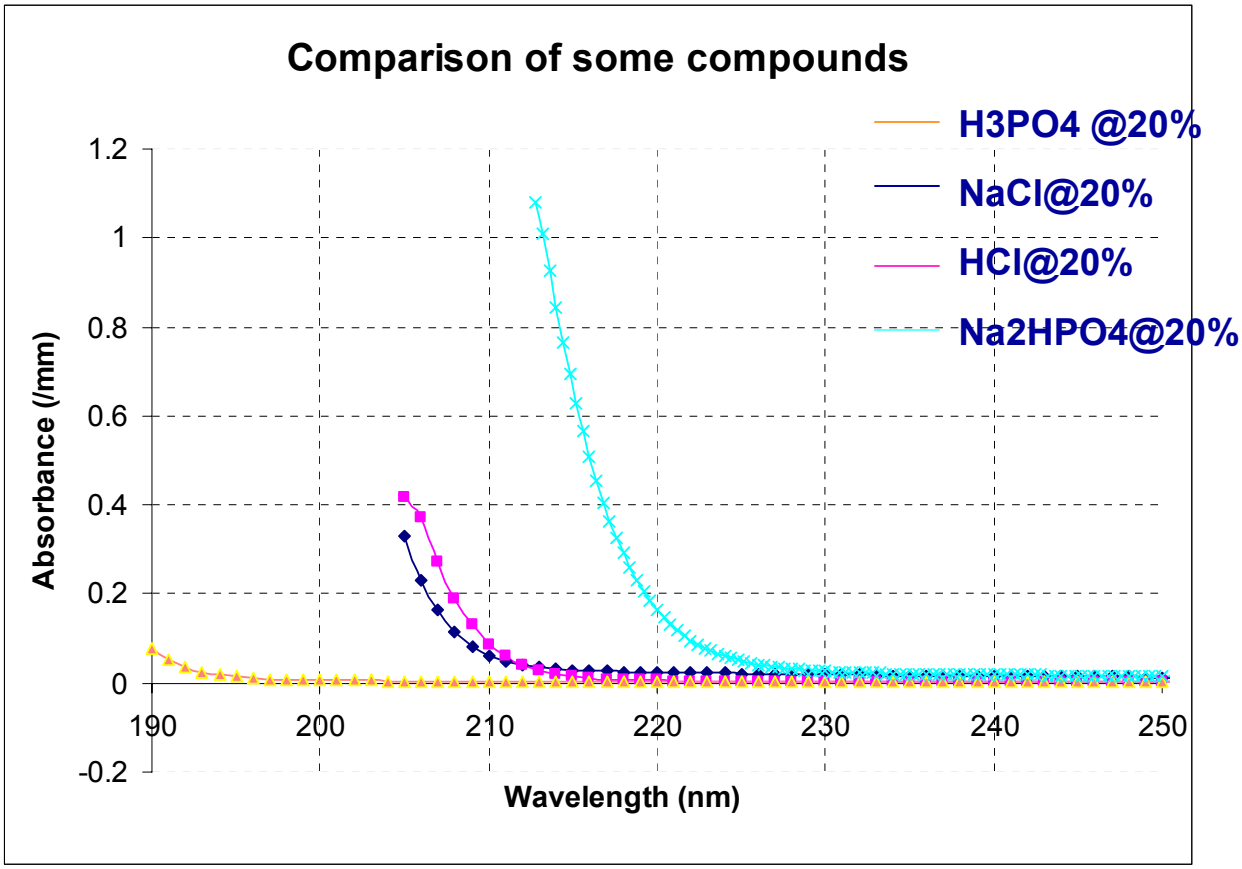
Various including M.J. Blandamer and M.F. Fox, Theory and Applications of Charge-Transfer-To-Solvent Spectra, (1968).

Compounds Studied



- **Halides: HCl, $AlCl_3$, $CaCl_2$, CsCl, CsI, KCl, $ZnBr_2$**
- **Sulfates: H_2SO_4, Li_2SO_4, Na_2SO_4, K_2SO_4, Rb_2SO_4, Cs_2SO_4, $Gd_2(SO4)_3$, $MgSO_4$, $ZnSO_4$ $AlK(SO_4)_2$, $AlNH_4(SO_4)_2$**
- **Phosphates: HsPO4, NaH2PO4, Na2HPO4, KH2PO4**
- **Nitrates: $Zn(NO_3)_2$**

Absorbance of Some Compounds



Fluid Absorbance at 193nm and 248nm

Fluids	λo (nm)	α(mm-1,@193nm)	α(mm-1,@248nm)
AlCl3·6H2O@50%	209	-	0.0103
HCl@20%	210	2.91*	0.0015
$CaCl_2$@20%	209	-	0.0257
CsCl@20%	206	-	0.0022
CsI@20%	-	-	-
KCl@20%	209	-	0.0031
$ZnBr_2$@20%	234	-	0.0129
$Zn(NO_3)_2$@40%	-	-	-
NaH_2PO_4@16%	196	0.429	0.110
Na_2HPO_4@16%	208	4.72*	0.0154
KH_2PO_4@16%	196	0.571*	0.163
H_3PO_4@20%	192	0.0251	0.00213

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

Fluid Absorbance at 193nm and 248nm

Fluids	λo (nm)	$\alpha(mm^{-1}$,@193nm)	$\alpha(mm^{-1}$,@248nm)
$AlK(SO_4)_2 \cdot 12H_2O$@20%	197	0.286	0.0048
$AlNH_4(SO_4)_2 \cdot 12H_2O$ (sat)	198	0.515	0.0024
H_2SO_4@20%	197	0.246	0.00183
Li_2SO_4@16%	228	-	0.0088
Na_2SO_4@17%	199	1.144*	0.0014
K_2SO_4@8%	199	1.03*	0.0006
Rb2SO4@25%	230	-	0.0229
Cs_2SO_4@40%	199	0.706	0.0017
$MgSO_4$@5%	196	1.05*	0
$Gd_2(SO_4)_3$@1.5%	195	0.0917	0
$ZnSO_4$@40%	201	-	0.0033

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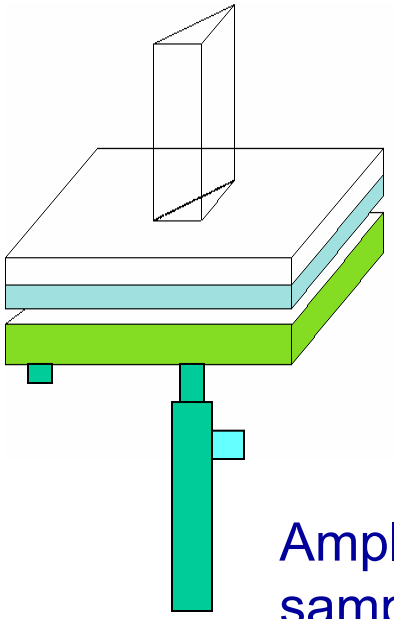
Prism Deviation Angle Experiment

- Fluid index and dispersion measurement needed for screening
- Measurement to $1x10^{-3}$ is adequate for initial work
- Refractometry methods are accurate to 10^{-3}~10^{-4}
- VASE tool provides an accurate goniometer and detector

Prism vial cell

Experimental setup with prism vial

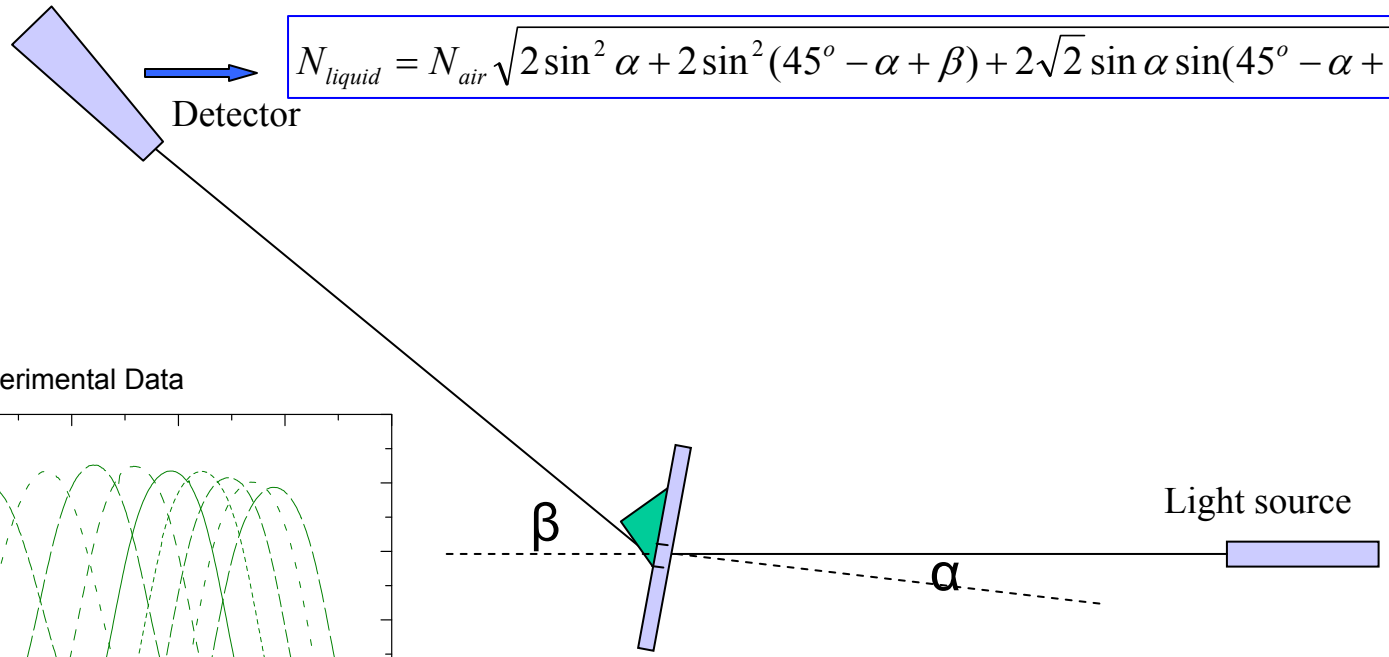


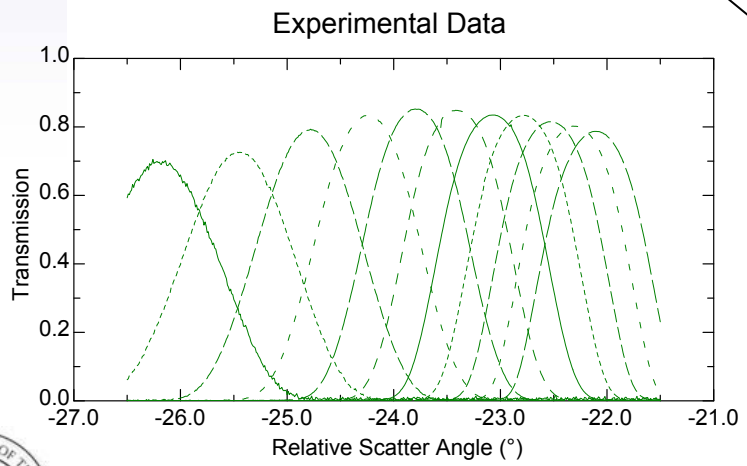
Amplified sample stage

Prism Deviation Angle Experiment

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

$$N_{liquid} = N_{air}\sqrt{2\sin^2\alpha + 2\sin^2(45^o-\alpha+\beta) + 2\sqrt{2}\sin\alpha\sin(45^o-\alpha+\beta)}$$





Fluid Refractive Index and Dispersion

Fluids	Refractive index @ 193nm	248nm	Cauchy parameters A	B	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
$AlCl_3 \cdot 6H_2O$@50%	1.5842	1.4894	1.4101	0.0024	0.000152
Hydrogen Phosphates					
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

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

Fluid Refractive Index and Dispersion

Fluids	Refractive index @ 193nm	Refractive index @ 248nm	Cauchy parameters A	Cauchy parameters B	Cauchy parameters C
$AlK(SO_4)_2 \cdot 12H_2O$@20%	1.4521	1.3988	1.3468	0.0021	0.0000686
$AlNH_4(SO_4)_2 \cdot 12H_2O$@20%	1.4374	1.3839	1.3329	0.0020	0.0000713
Li_2SO_4@16%	1.4559	1.4032	1.35	0.00224	0.0000635
Rb_2SO_4@25%	1.4557	1.4020	1.35	0.0021	0.0000695
$ZnSO_4$@40%	1.4819	1.4243	1.3678	0.0022	0.0000754
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
Na_2SO_4@30%	1.479	1.423	1.3667	0.0023	0.000069
$NaHSO_4$@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
H_2O (DI)	1.435	1.373	1.3283	0.0021	0.000067

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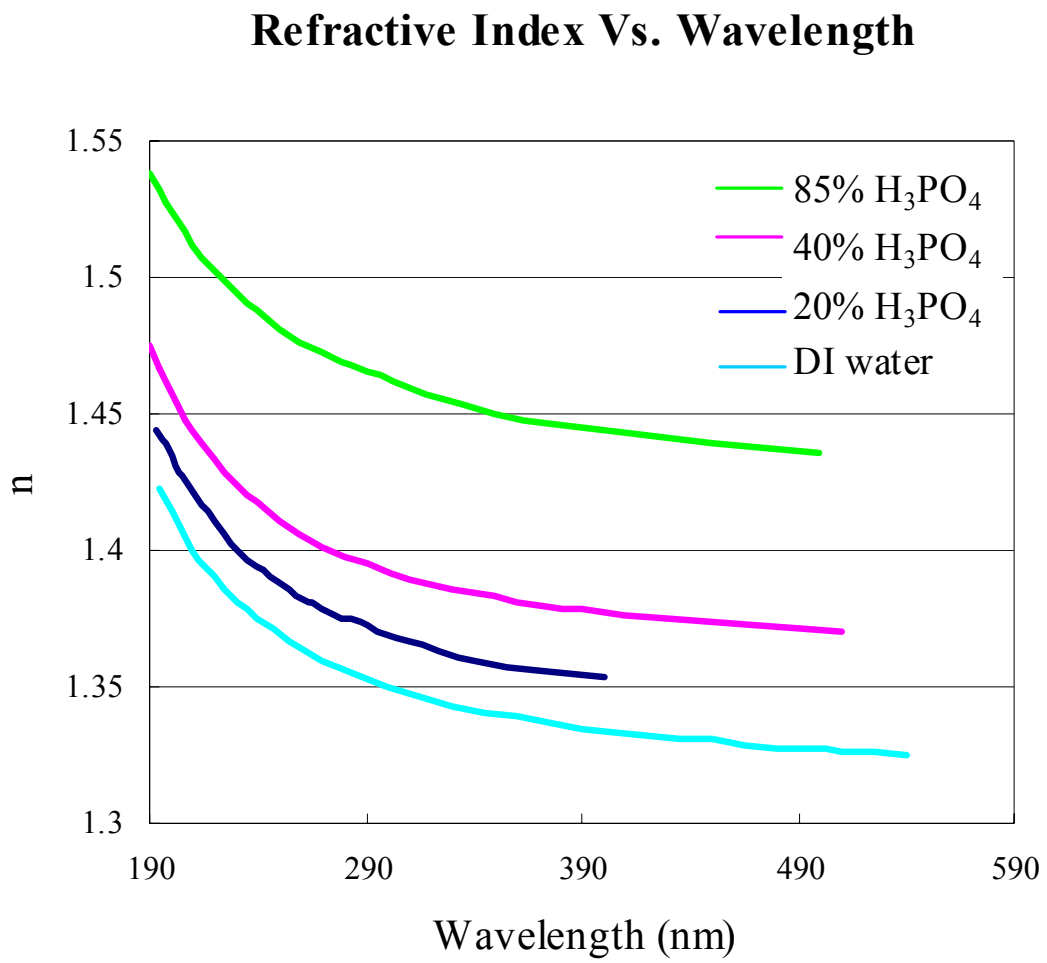
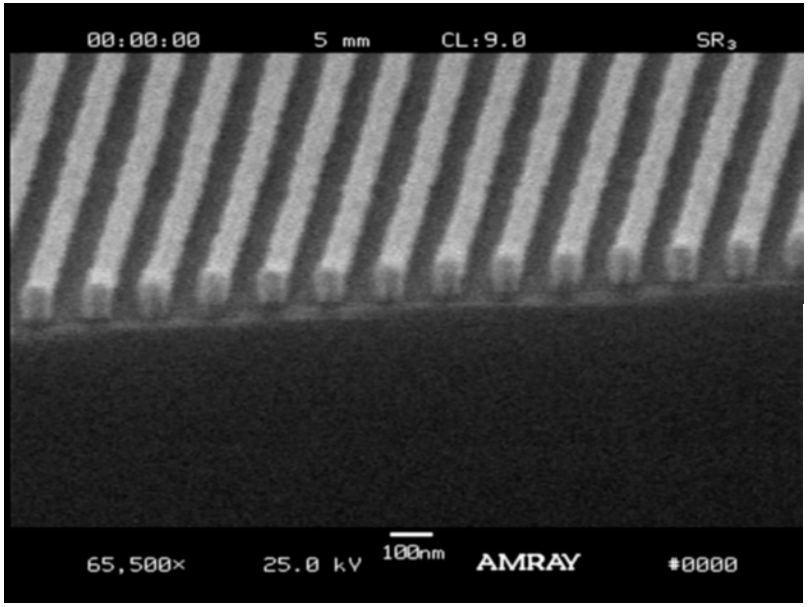
Measured Refractive Index of Phosphoric Acid



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 and Future Work

- Fluid absorption is driven by excitation of electron from ground state to molecular electronic state
- Deviation Angle Experiment gives accurate results
- Phosphates were found to have higher refractive index than DI water
- Immersion lithography results using 40% and 85% H_3PO_4 have been demonstrated
- Some more liquids will be tried
- Data available at: http://www.microe.rit.edu/research/lithography/