Ozonolysis of Organic Photoresist
Direct or Indirect?
Fundamental Mechanisms

Environmentally Benign Semiconductor
Manufacturing Research Center

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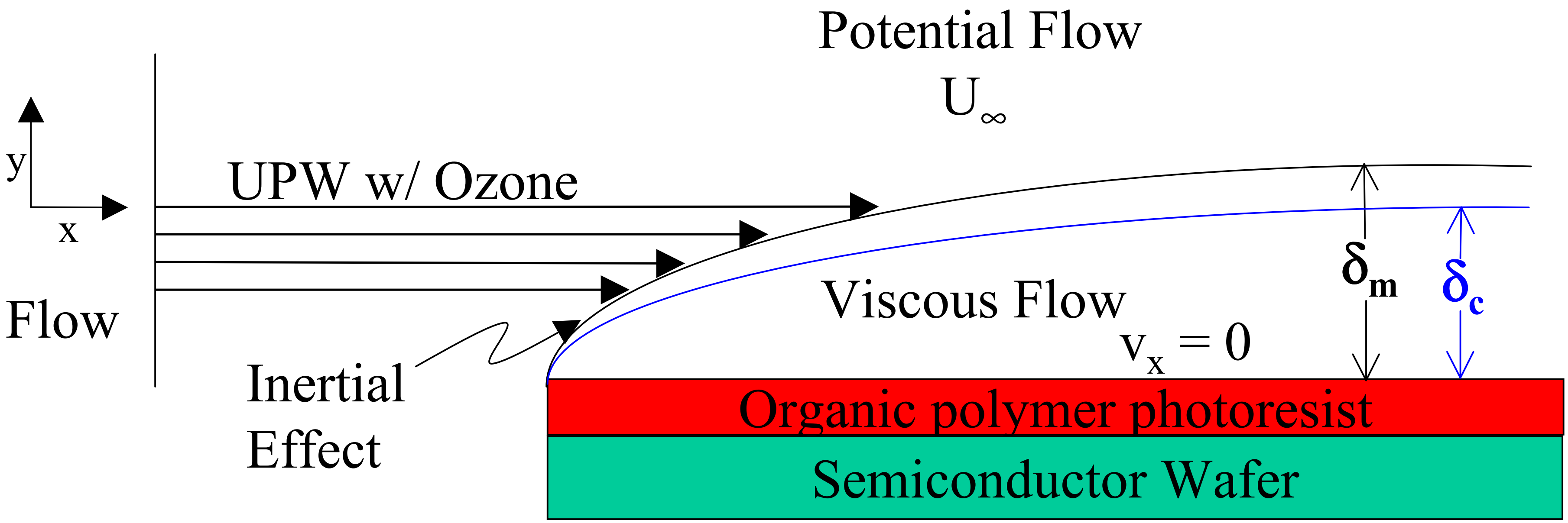


$$\tau_{yx} = - \mu \frac{\delta v_x}{\delta y}$$

Boundary Conditions:

@ $x = 0$; $v_x = U_\infty$; for all $y > 0$

@ $y = 0$; $v_x = v_y = 0$; no slip condition

@ $y = \infty$; $v_x = U_\infty$, $v_y = 0$; a flat plate scenario

For Ultrapure Water, the Schmidt number, $Sc \cong 1000 >> 1$.

Mass Transfer Equations

Continuity Equation:

$$\frac{\delta v_x}{\delta x} + \frac{\delta v_y}{\delta y} = 0$$

Conservation of Momentum:

X momentum;

$$\rho\left(\frac{\delta v_x}{\delta t} + v_x\frac{\delta v_x}{\delta x} + v_y\frac{\delta v_x}{\delta y}\right) = -\frac{dP}{dx} + \mu\left(\frac{\delta^2 v_x}{\delta x^2} + \frac{\delta^2 v_x}{\delta y^2}\right) + \rho g$$

Conservation of Mass:

$$\frac{\delta C_{O_3}}{\delta t} + v_x\frac{\delta C_{O_3}}{\delta x} + v_y\frac{\delta C_{O_3}}{\delta y} = D_{O_3/H_2O}\left(\frac{\delta^2 C_{O_3}}{\delta x^2} + \frac{\delta^2 C_{O_3}}{\delta y^2}\right)$$

These equations can be solved for the Flux of Ozone through the boundary layer, by determining the concentration boundary layer thickness $\boldsymbol{\delta_c}$. This can be determined from a scale analysis relative to the momentum boundary layer thickness $\boldsymbol{\delta_m}$.

Combining the equation of motion with the continuity equation;

setting $\eta = y(U_\infty / \mu x)^{1/2} = 5$

using a boundary layer velocity of $v_{bl} = 0.99\ U_\infty$

$$\frac{\delta_m}{x} = \frac{5}{(Re)^{1/2}}$$

For steady state conditions, w/ an incompressible fluid and a steady stream, the x momentum equation can also be simplified to;

$$\mathbf{v_x \frac{\delta v_x}{\delta x} + v_y \frac{\delta v_x}{\delta y} = \nu \frac{\delta^2 v_x}{\delta y^2}}$$

Combining this Equation of Motion with the Continuity Equation, for $y \ll \delta_m$, using the combination of variables technique, these equations can be solved to yield;

$$\mathbf{v_x \cong \frac{U_\infty y}{\delta_m}}$$

$$\mathbf{v_y \cong \frac{\nu y^2}{\delta_m^{\ 3}}}$$ **Very near the plate.**

The Conservation of Mass equation simplifies to;

$$v_x \frac{\delta C_{O_3}}{\delta x} + v_y \frac{\delta C_{O_3}}{\delta y} = D_{O_3/H_2O} \frac{\delta^2 C_{O_3}}{\delta y^2}$$

The concentration boundary layer thickness, δ_c, can be estimated from a scale analysis with the momentum boundary layer thickness, δ_m.

This leads to;

$$\delta_c = \frac{\delta_m}{(Sc)^{1/3}}$$

$$\frac{\delta_c}{x} = \frac{1}{(Re)^{1/2}\,(Sc)^{1/3}}$$

Ozone Flux: $$N_{O_3} = \frac{-D_{O_3/H_2O}}{\delta_c} C_{O_3}$$

Ozone/Water Chemistry

$$O_3 + H_2O \xrightleftharpoons{\text{High pH}} O_2 + 2OH^*$$ **pH controlled**

$$O_3 + OH^* \rightleftharpoons O_2 + HO_2^*$$

$$O_3 + HO_2^* \rightleftharpoons OH^- + 2O_2$$

$$O_3 + OH^- \rightleftharpoons HO_2^- + O_2$$

$$O_3 + HO_2^- \rightleftharpoons OH^* + {}^*O_2^- + O_2$$

$$O_3 + {}^*O_2^- \rightleftharpoons {}^*O_3^- + O_2$$

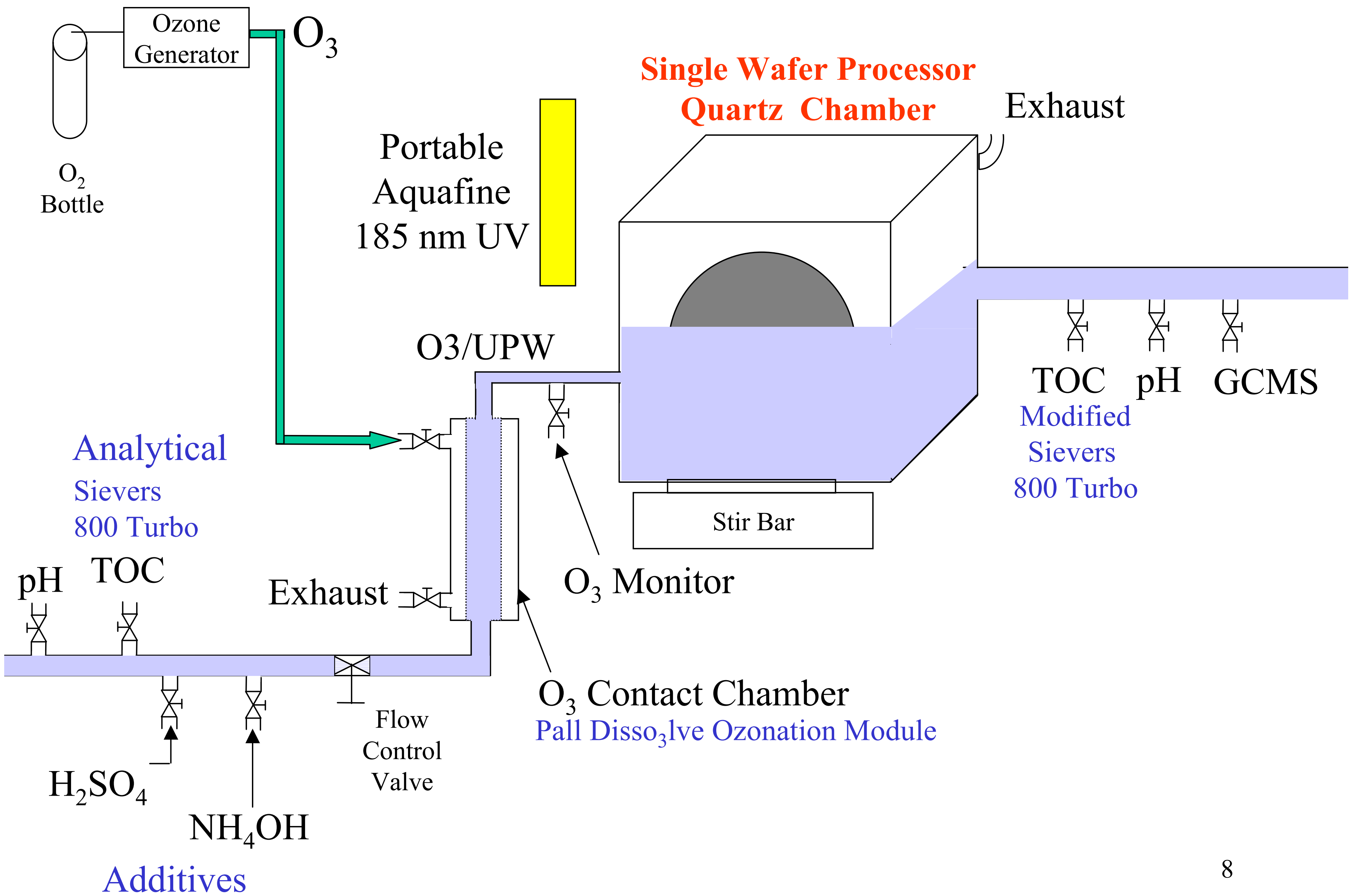
$$ {}^*O_3^- + H_2O \rightleftharpoons OH^- + OH^* + O_2$$

$$OH^*, HO_2^*, {}^*O_2^-, {}^*O_3^-, O_3 + CH_n \longrightarrow CH_m + CO_2 + H_2O$$

Published data indicates oxidation of 10 - 25% of C bonds in PR.
Industry adds radical scavengers to suppress radical reactions.
Radicals are superior oxidizing agents relative to ozone.
O_3 will not attack C--C single bonds, radicals will.
Can the radicals be used to oxidize the PR?

Plans: **Selectively form radical at wafer surface, not in bulk sol'n.**
Form high pH/OH environment on wafer surface,
Apply O_3/UPW at low pH with acid prefeed,
Generate radicals near organics in boundary layer.
Model mass transfer/kinetics.

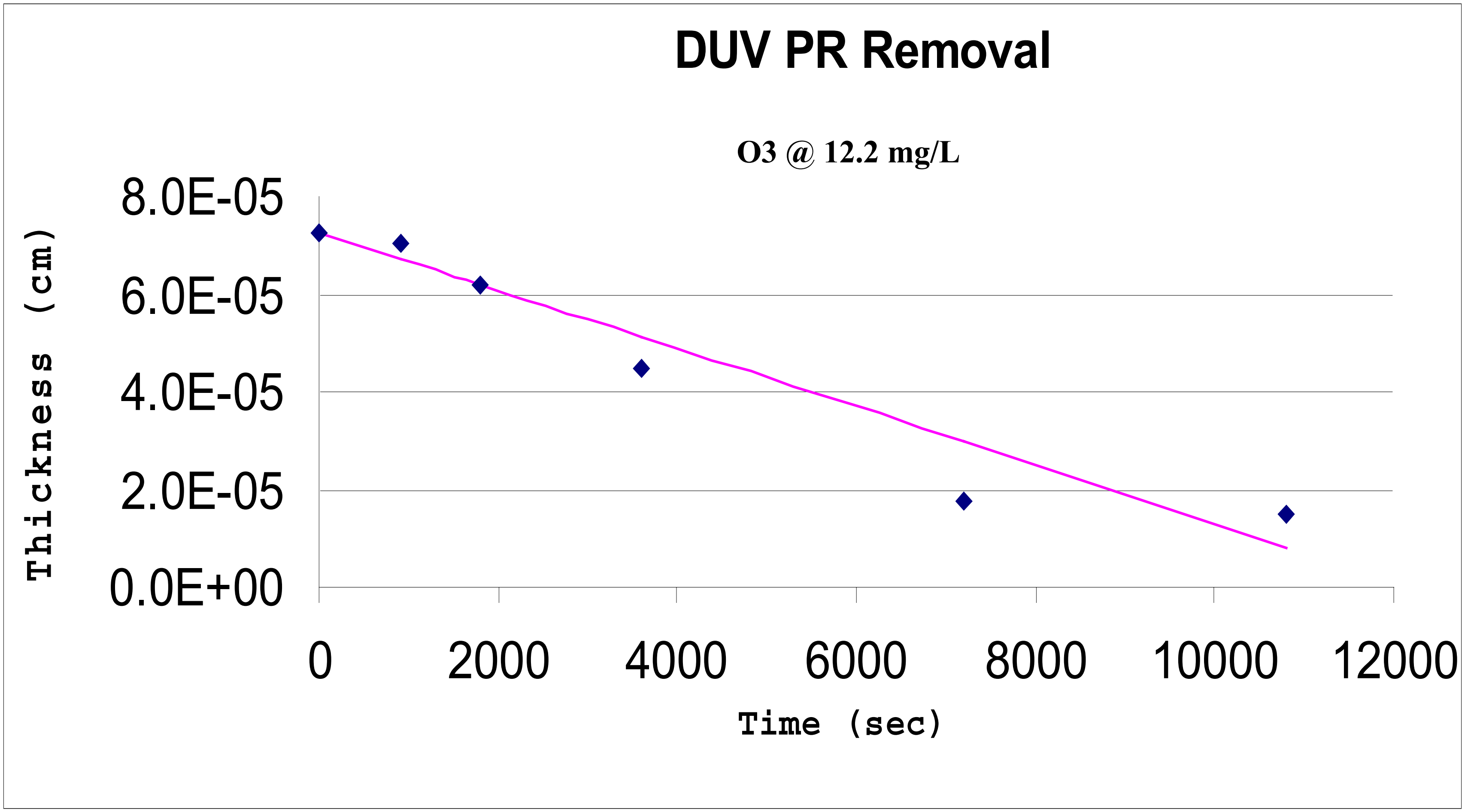
Experimental Setup



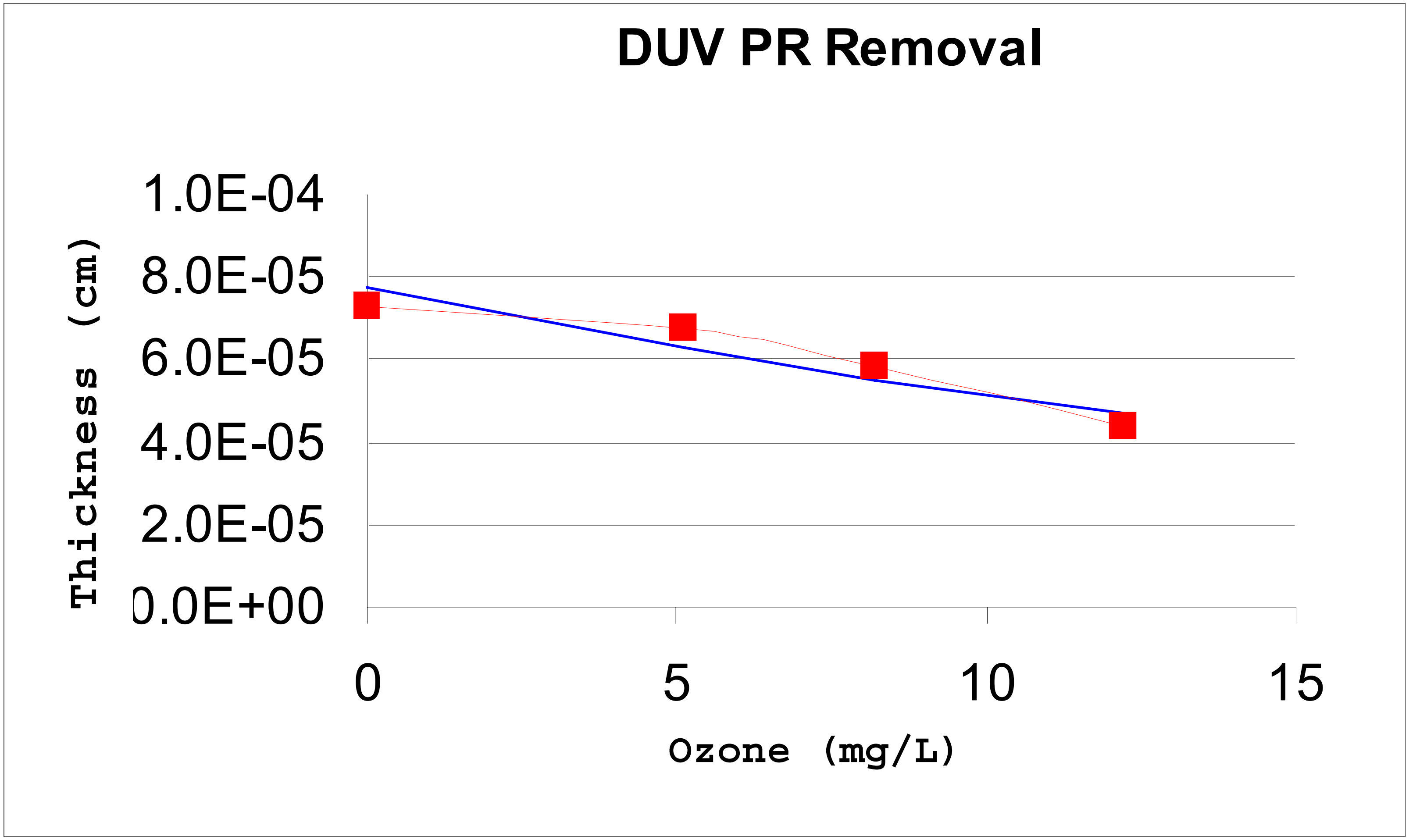
Quartz Tank Reactor

#	Wafer Pretreatment									UPW Pretreatment			Treatments						
#	Broad UV	185 nm UV	2.38% TMAH Soak 30 min	28% NH4OH Soak 30 min	10% NaOH Soak 1 sec	1% NaOH Soak 30 min	10% H2O2 Soak 30 min	100% Acetic Acid 1 sec	12% Acetic Acid 30 min	pH 2-3 w/ H2SO4	pH 10-11 w/ NH4OH	28% H2O2 1mL/min to 1L/min	Quiescent O3/UPW Bath	O3/UPW Sprayed Onto Dry Wafer	O3/UPW Flowing (1 L/min)	O3 (mg/L)	UV-UPW-O3 (1L/min)	UV-H2O (1L/min)	Stir Bar
1													■			8.1			
2														■		8.1			
3															■	12.1			
4															■	12.1			7
5	■		■												■	12.1			7
6	■														■	12.1			7
7			■												■	12.1			7
8															■	12.1			7
9				■						■					■	16.4			7
10										■					■	16.4			7
11	■		■												■	0.0			
12		■	■												■	16.4			7
13				■											■	8.2			7
14				■											■				7
16						■									■	16.4			7
17										■					■	16.8			7
18		■													■	9.2			7
19								■							■	0.0			0
20									■						■	8.1			7
21						■									■	8.1			7
22											■					1.1		■	
23												■				0.9		■	
24							■											■	7
25															■	12.2	■		7
26													■			3.9			
27														■		3.4			
28															■	2.8			
29															■	2.2			7
30															■	5.1			
31															■	8.2			
32															■	12.2			
33															■	12.2			
34															■	12.2			
35															■	12.2			
36															■	12.2			
37															■	12.2			
38															■	12.2			
39															■	12.2			
40															■	12.2			

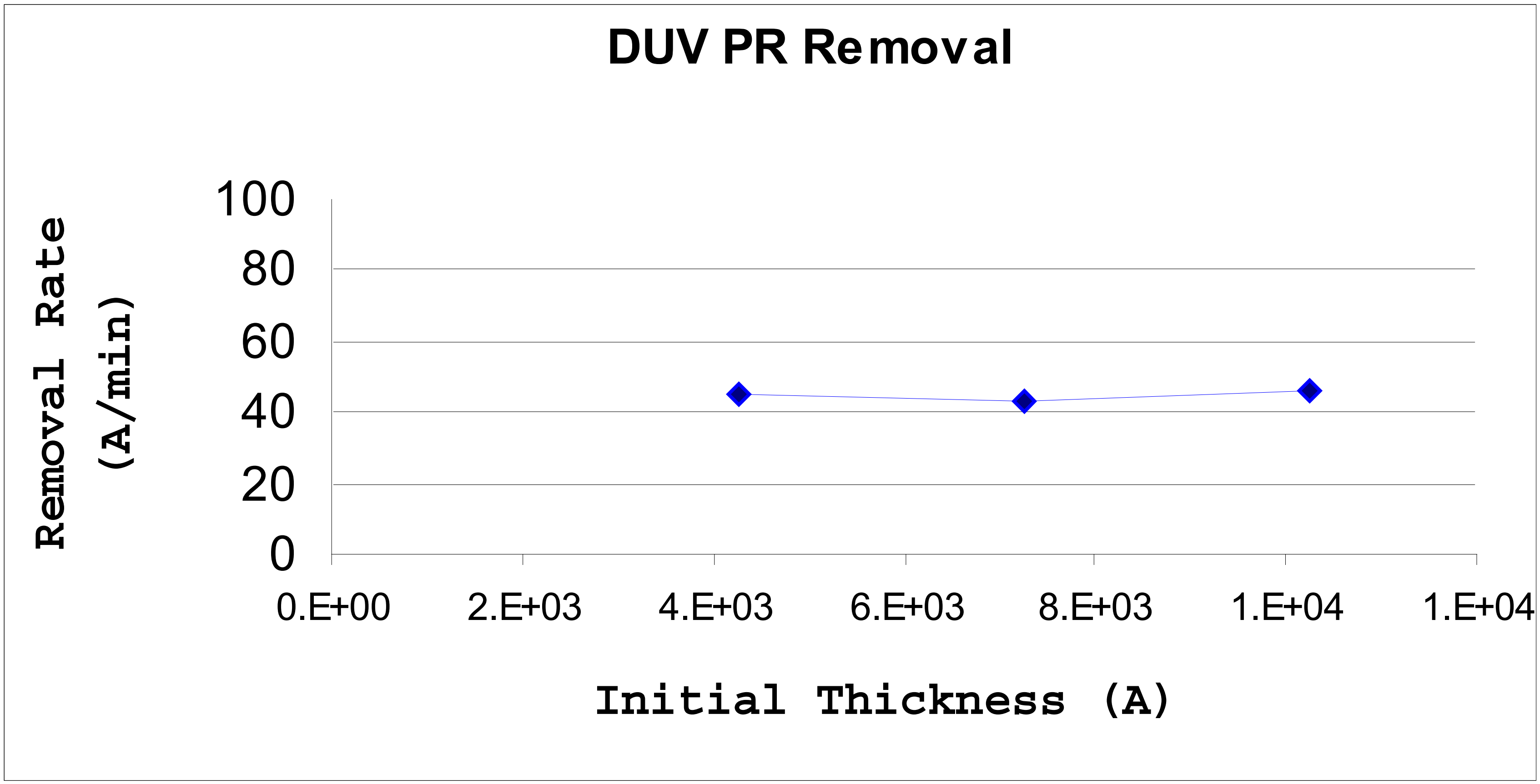
DUV PR Removal Rates
Initial Thickness vs Time



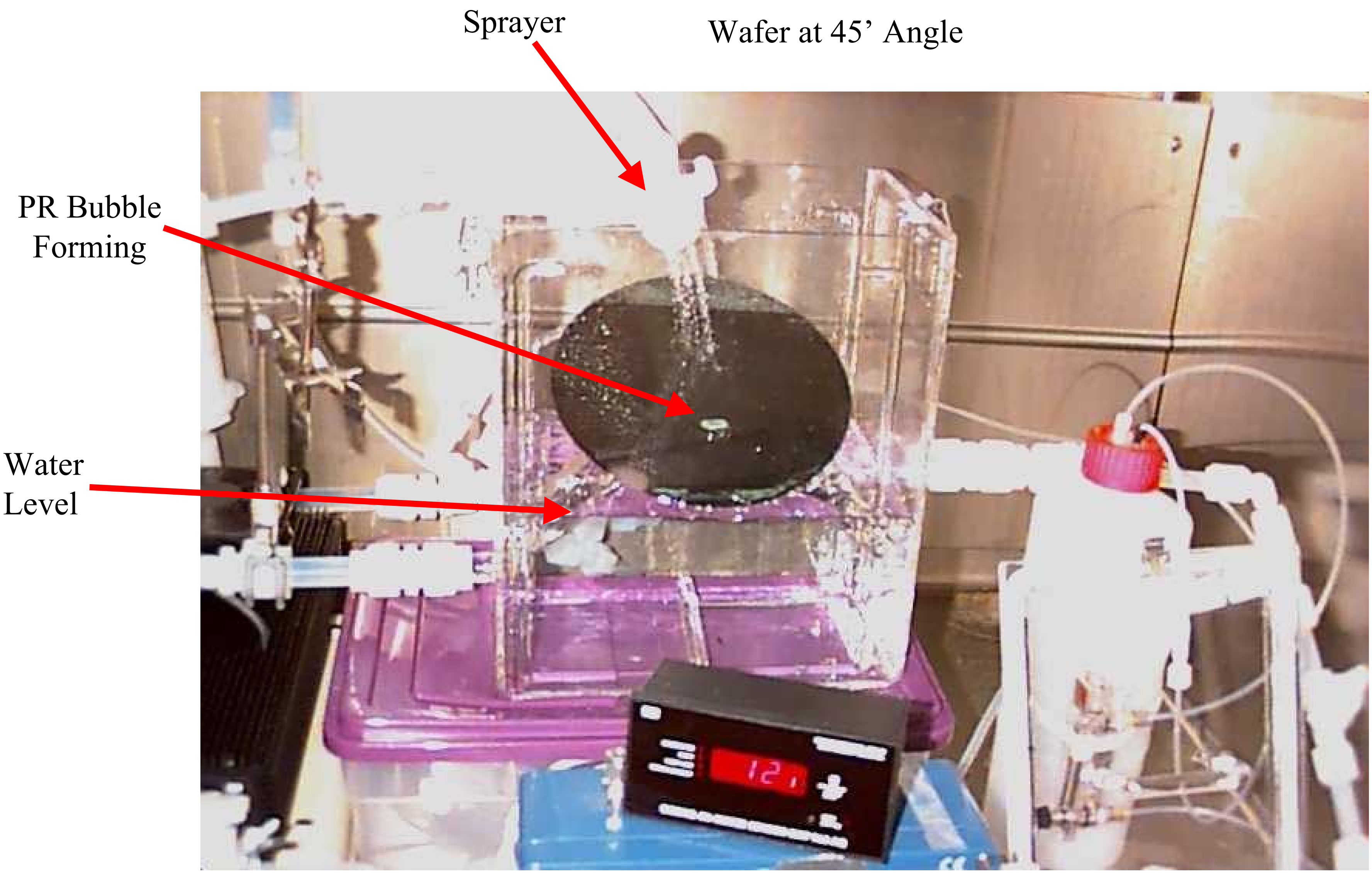
DUV PR Removal Rates
Final Thickness vs O_3 Concnetration



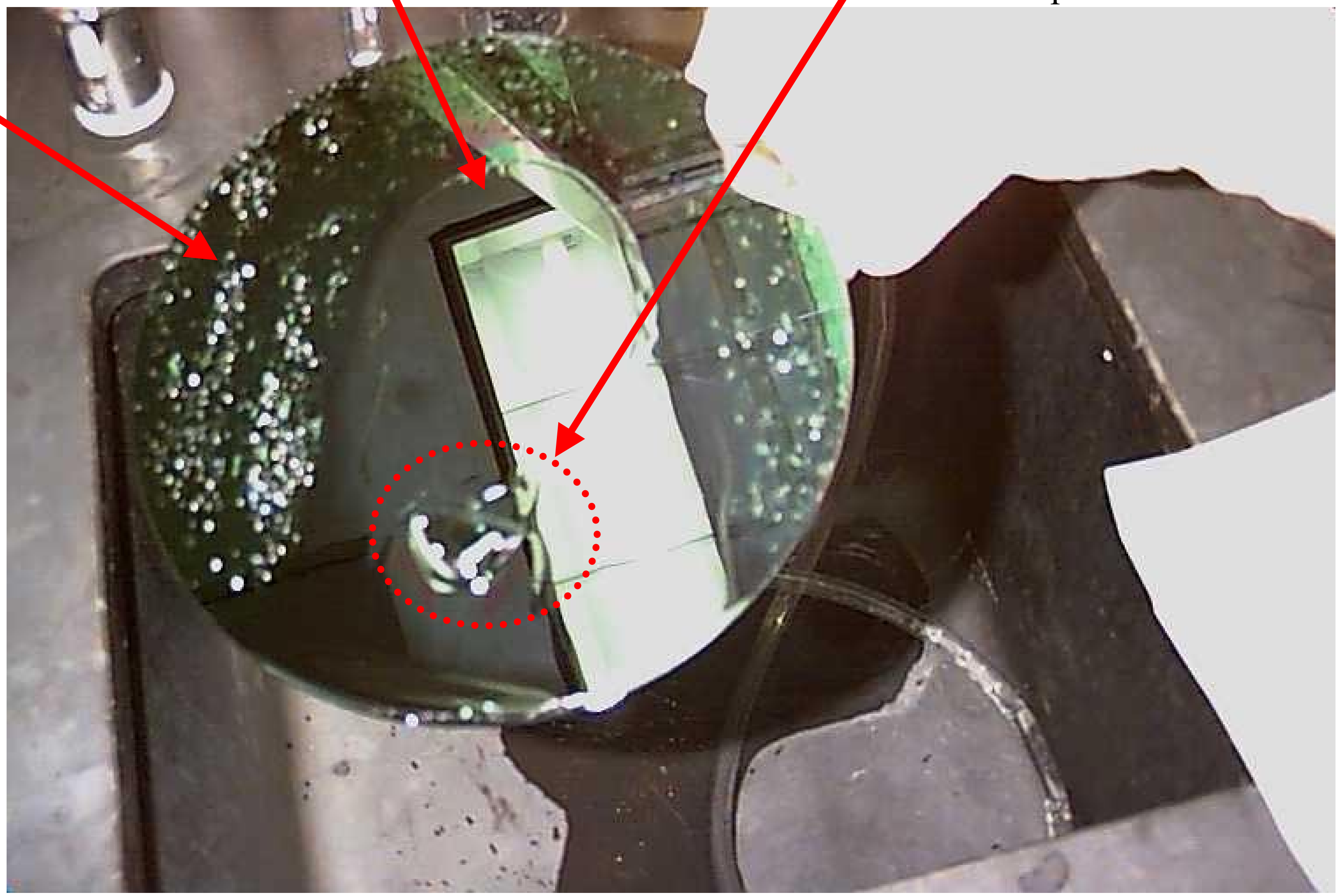
DUV PR Removal Rates
Removal Rate vs. Initial Thickness



Spray Tank Set UP

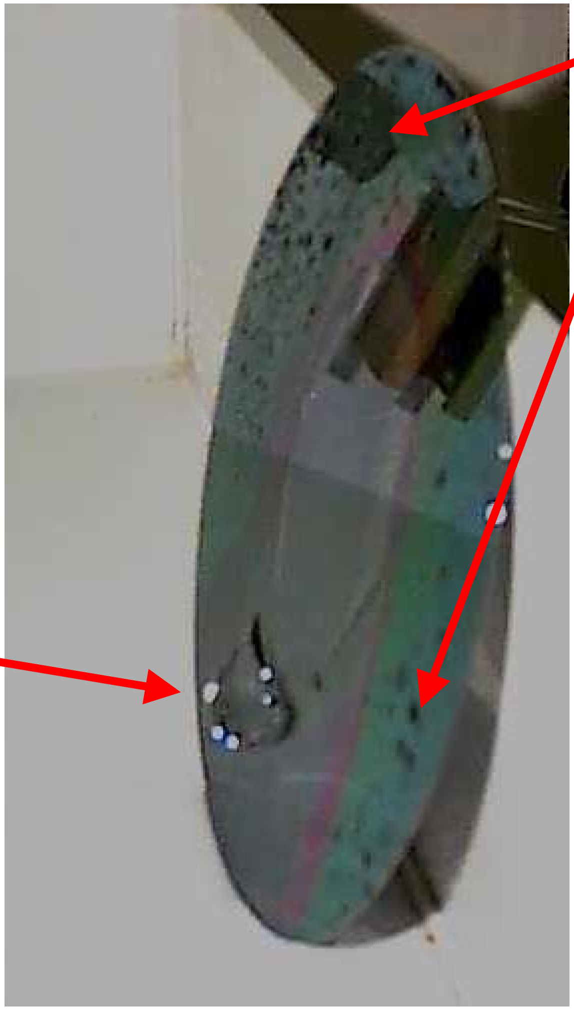


Wet Wafer
After processing



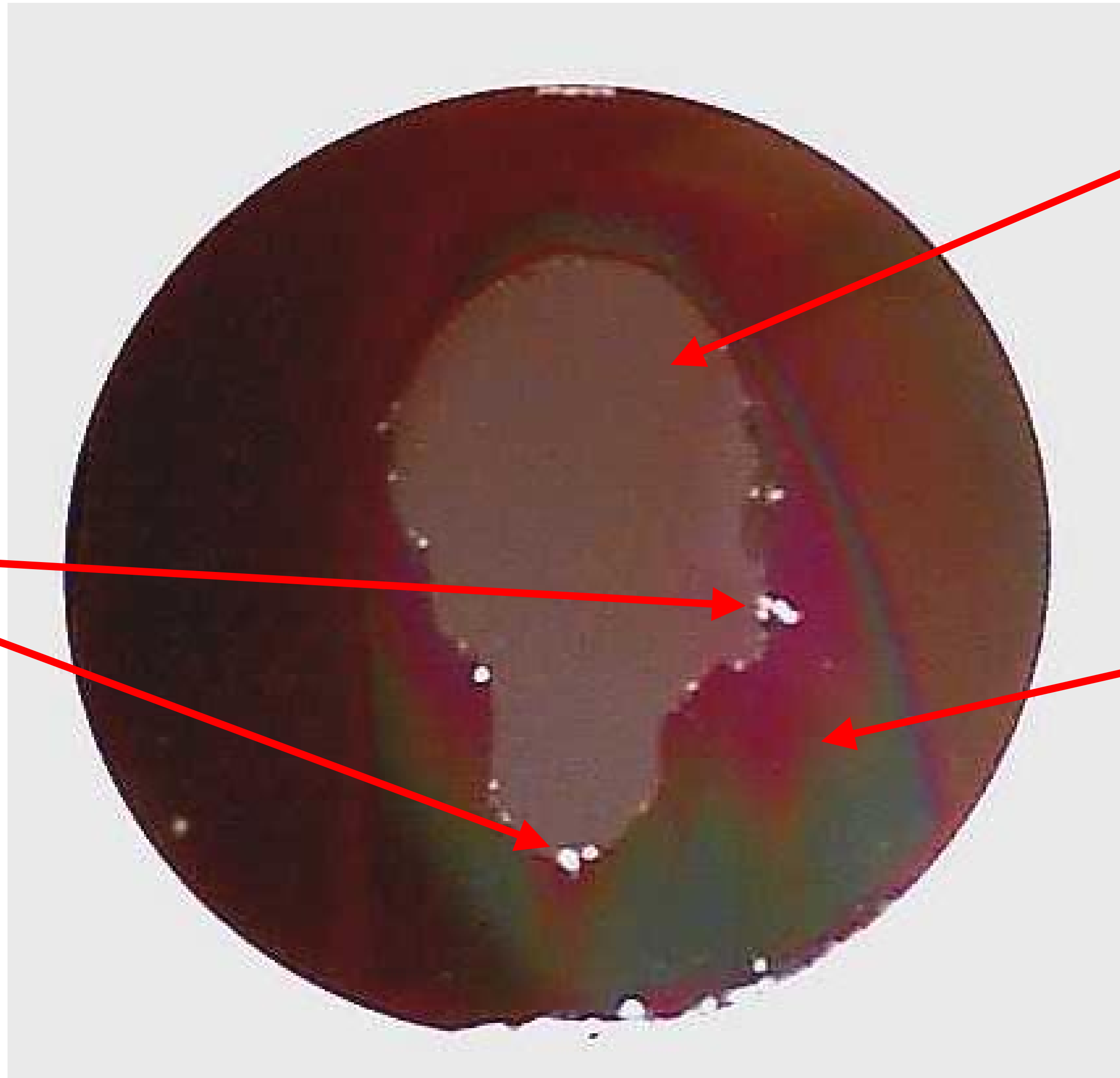
Wet Wafer
after processing
Side View

Water beads
on PR coated
areas



Large PR bubble
formation
at bottom
full of water

Dry Wafer
after processing

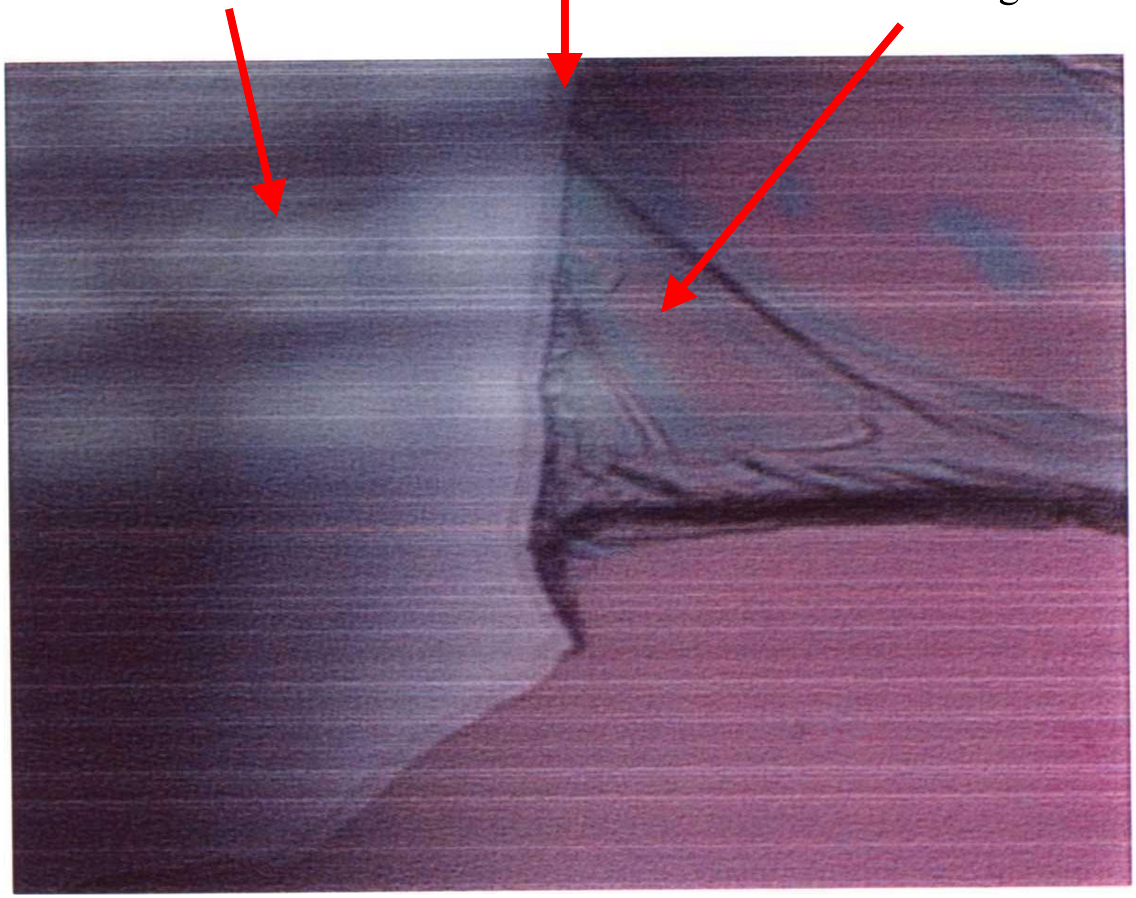


Reflective areas are pockets where PR has lifted

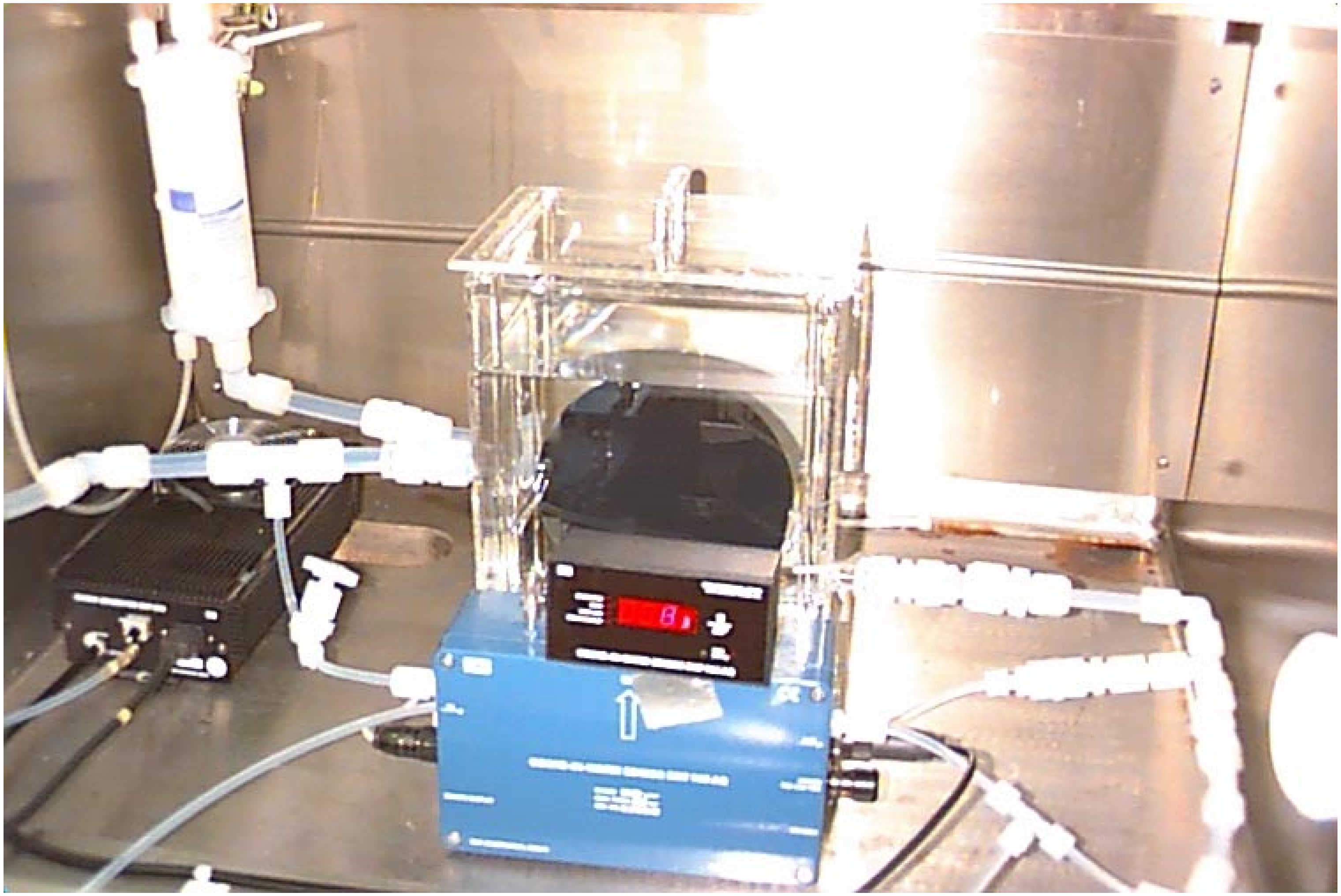
PR Removal Area

Discolorization of PR

Expanded Area



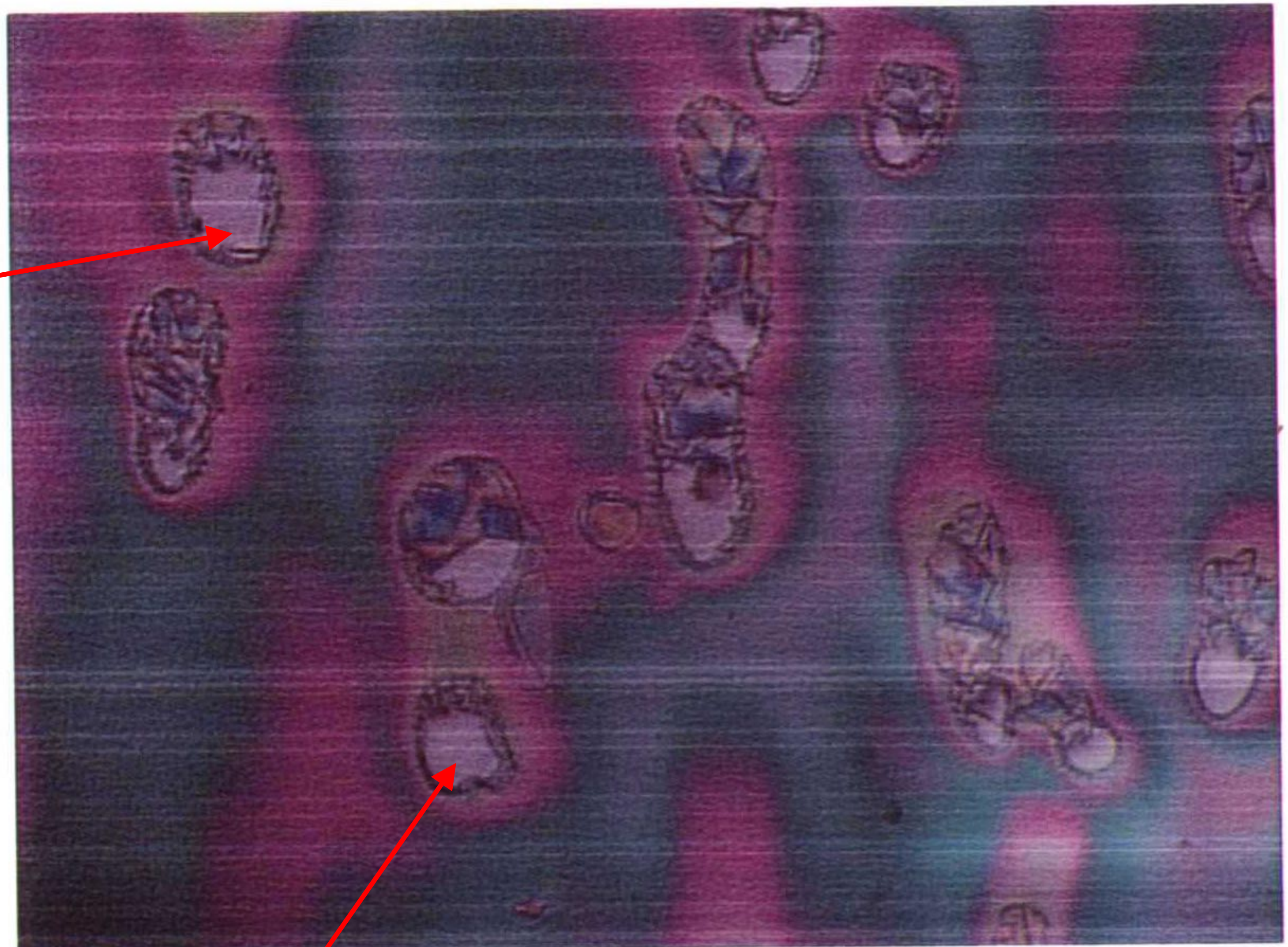
Experimental Setup



Bubble Formation PR Oxidation

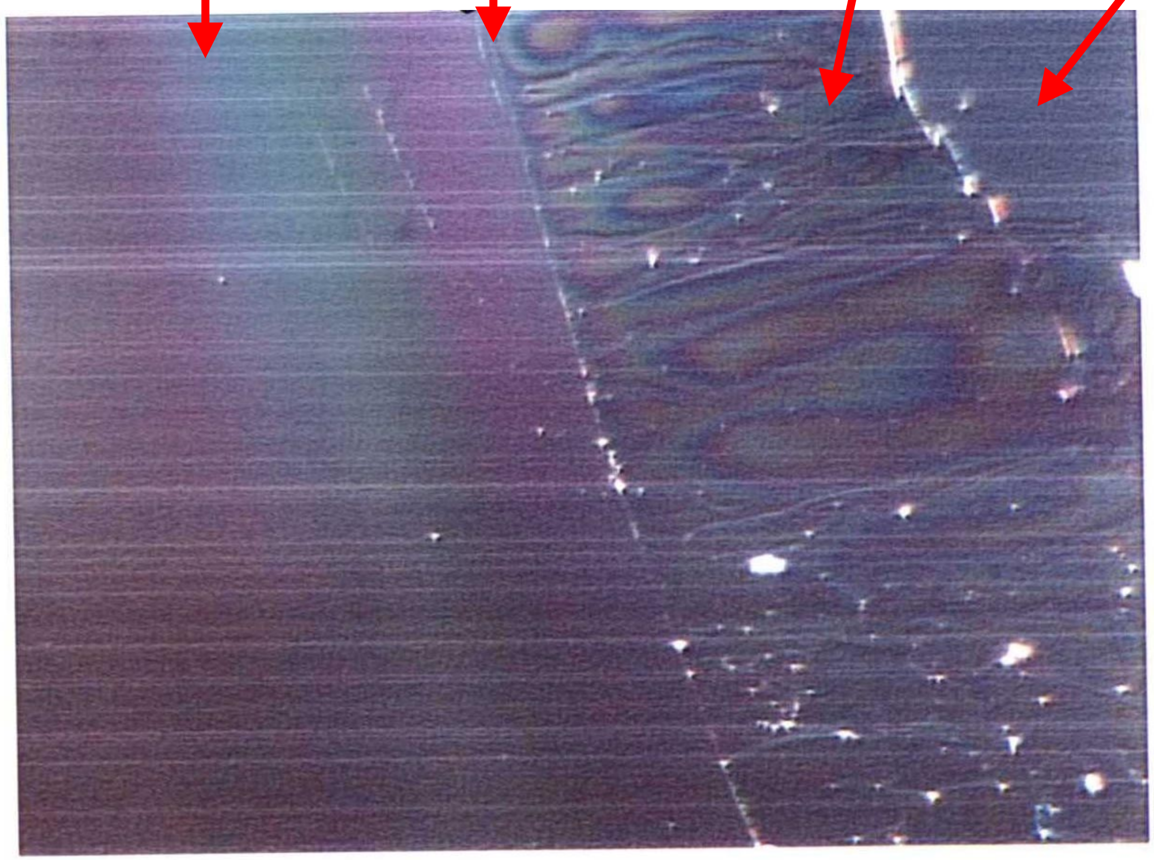
Top of Wafer

Bubble location

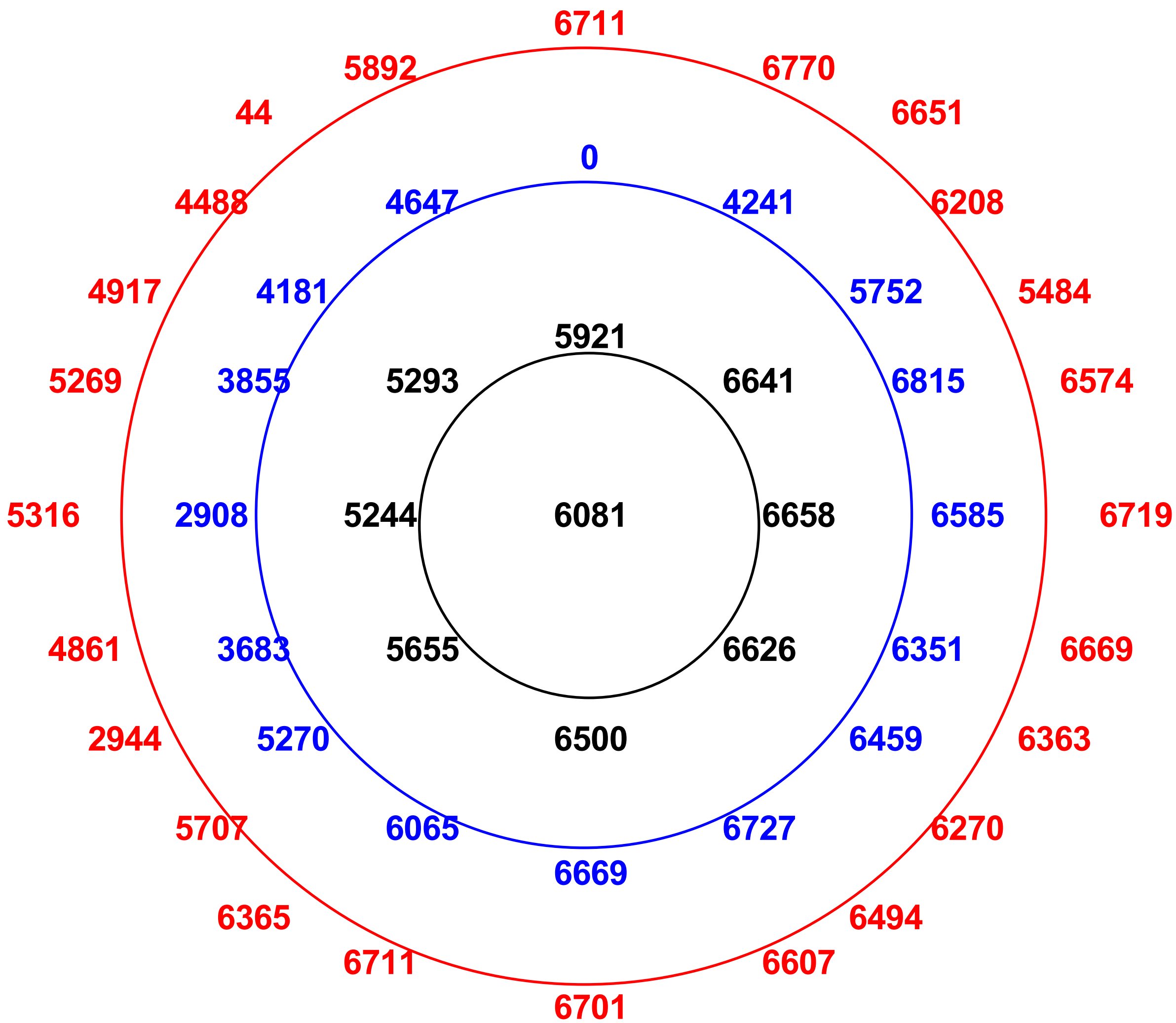


Bubble location

Expanded Bubble Area



Wafer 6



Left Average = 4729 Right Average = 6365

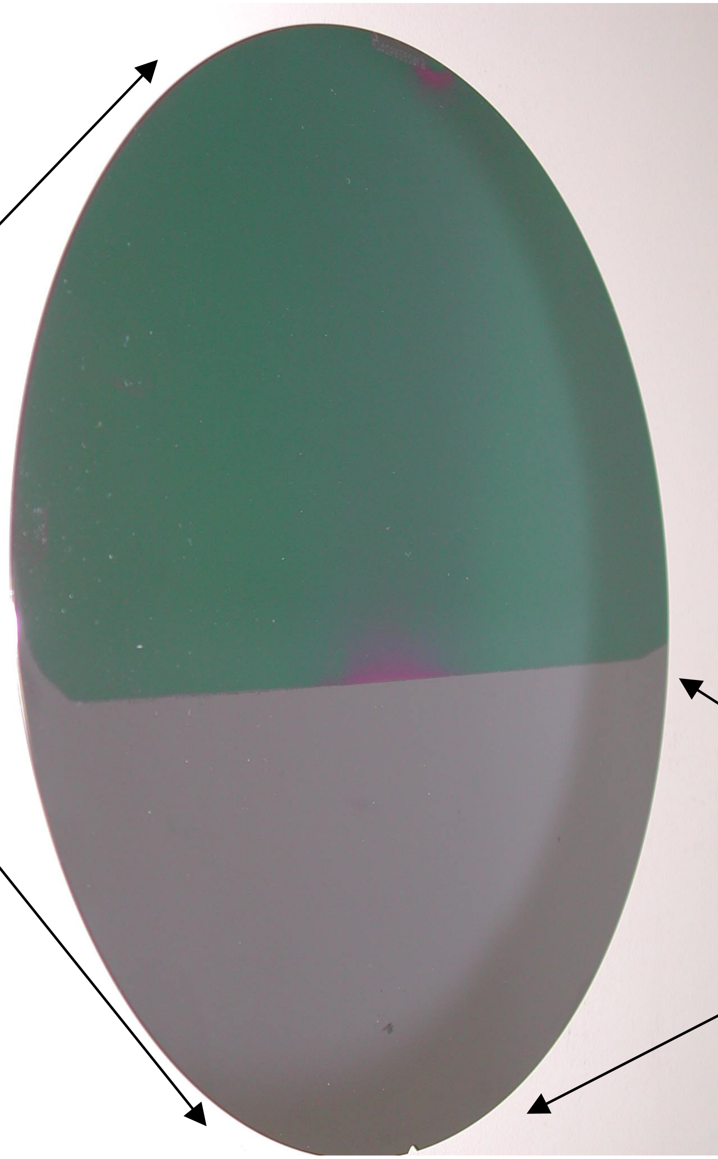
Rate 42 15

Average = 5542

Rate 29

Broad UV, 2.38% NH4OH, O3/UPW

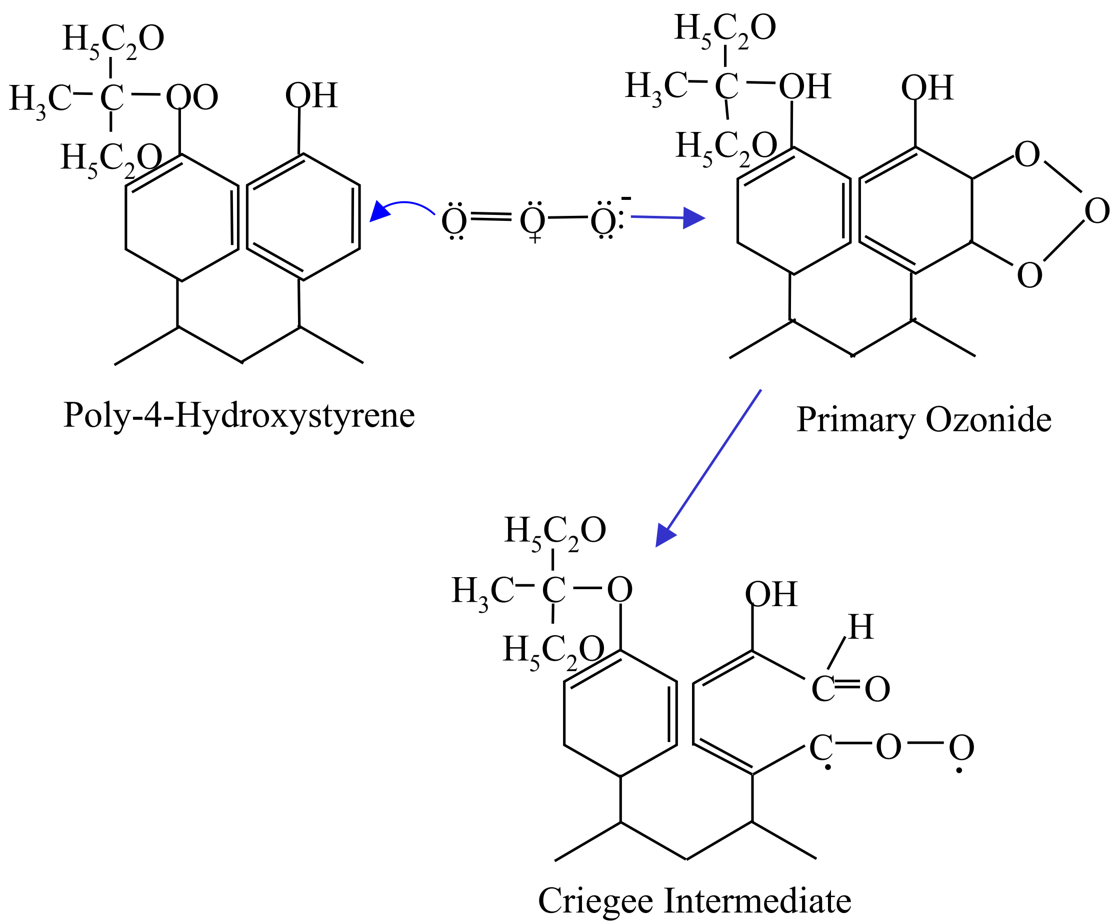
Broad UV Exposure 5 days



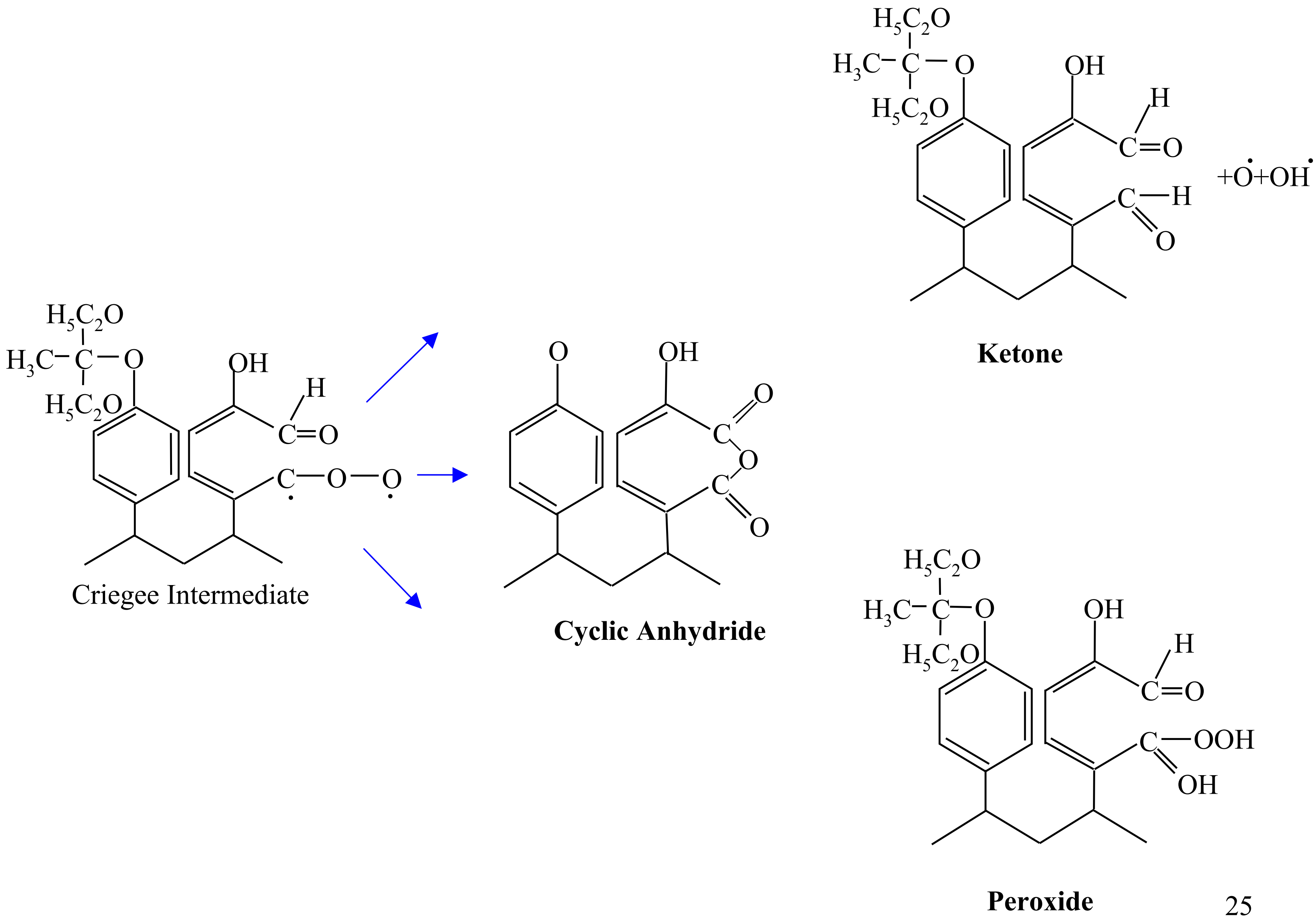
Entire Wafer Immersed in UPW for 60 min.

TMAH Exposure 30 min.

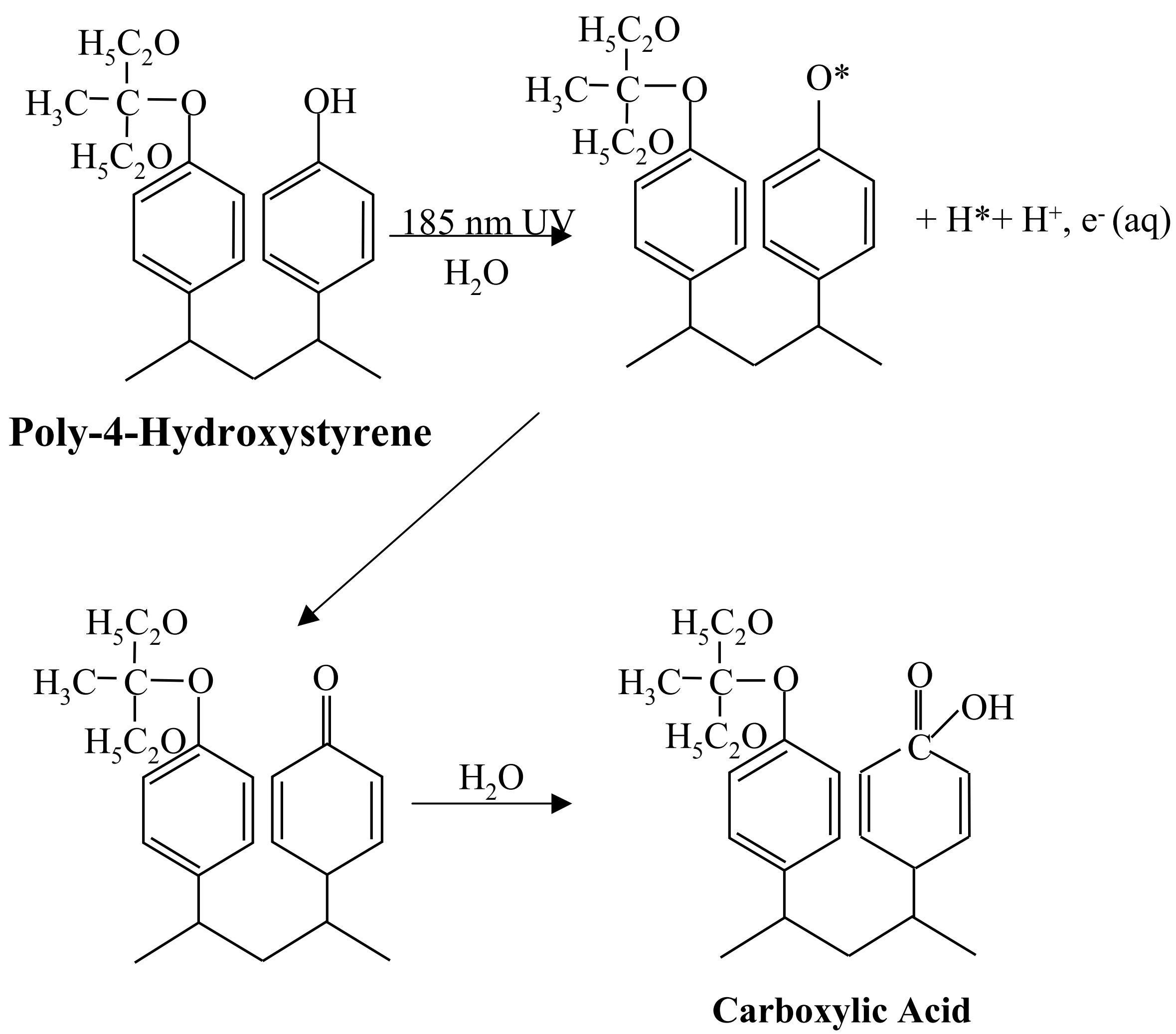
Ozone attack on PHS
Criegee Intermediate Formation



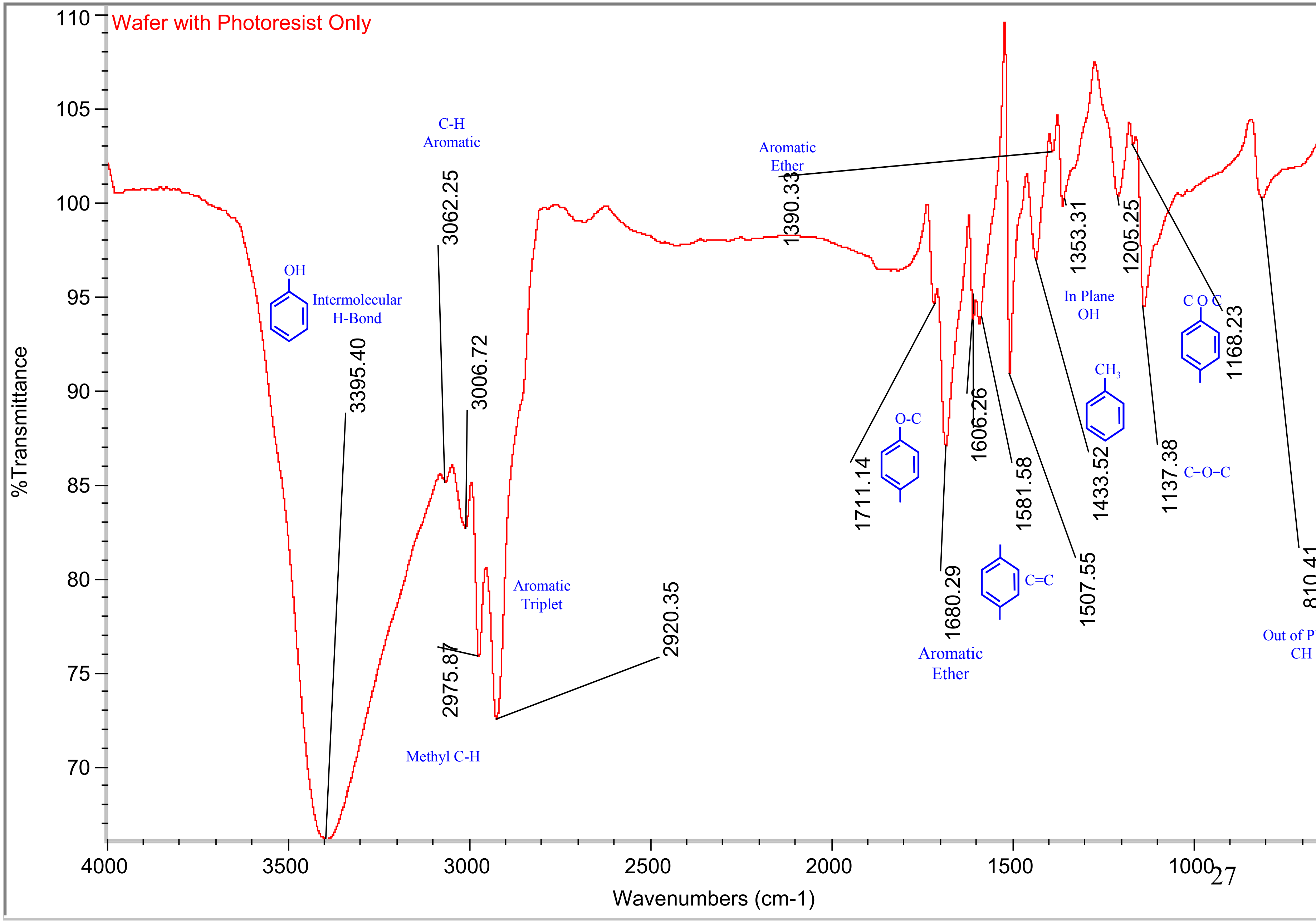
Ozone attack on PHS: Ketone, Anhydride, Peroxides



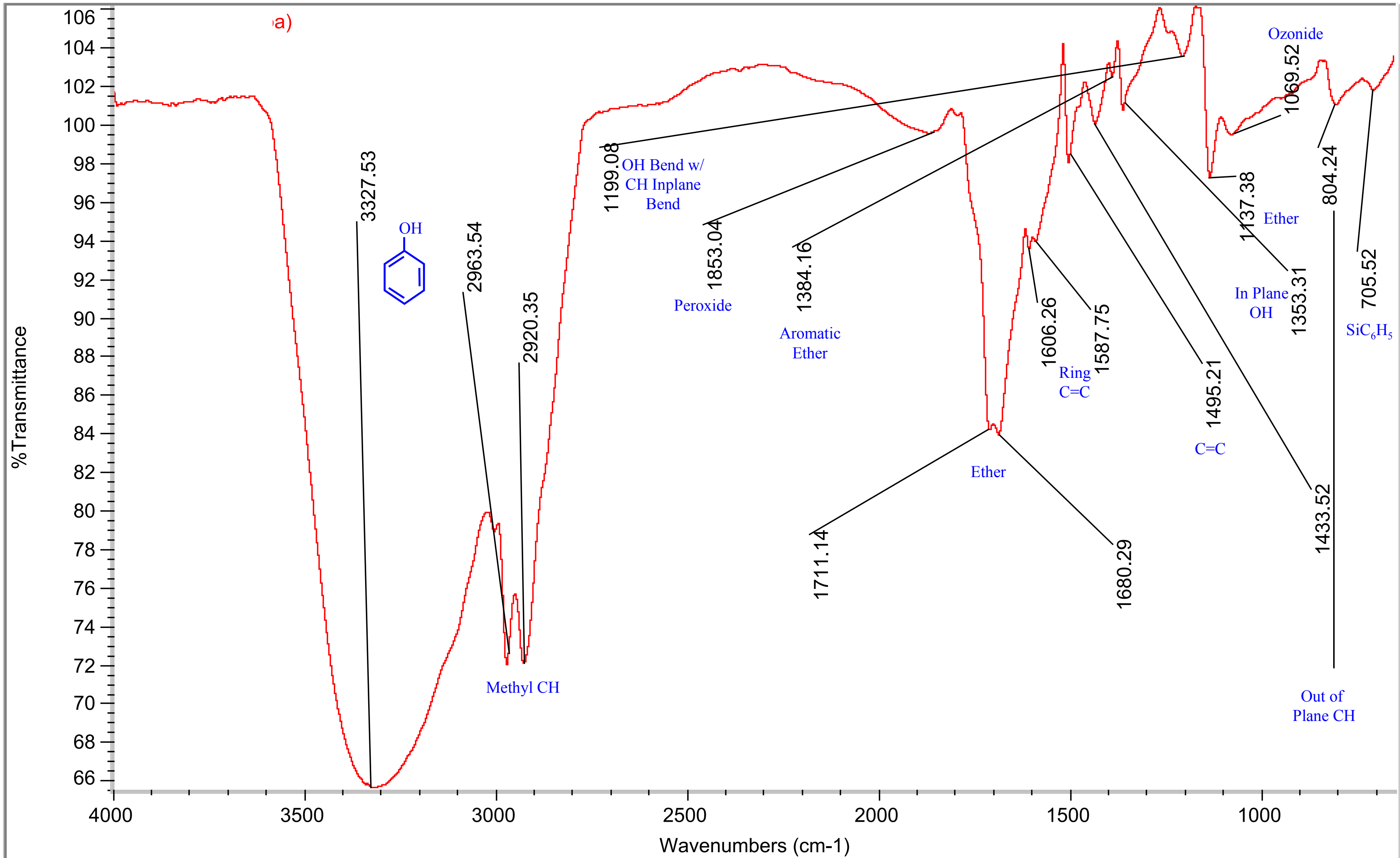
Hydroxyl Radical Attack; Carboxylic Acid Formation



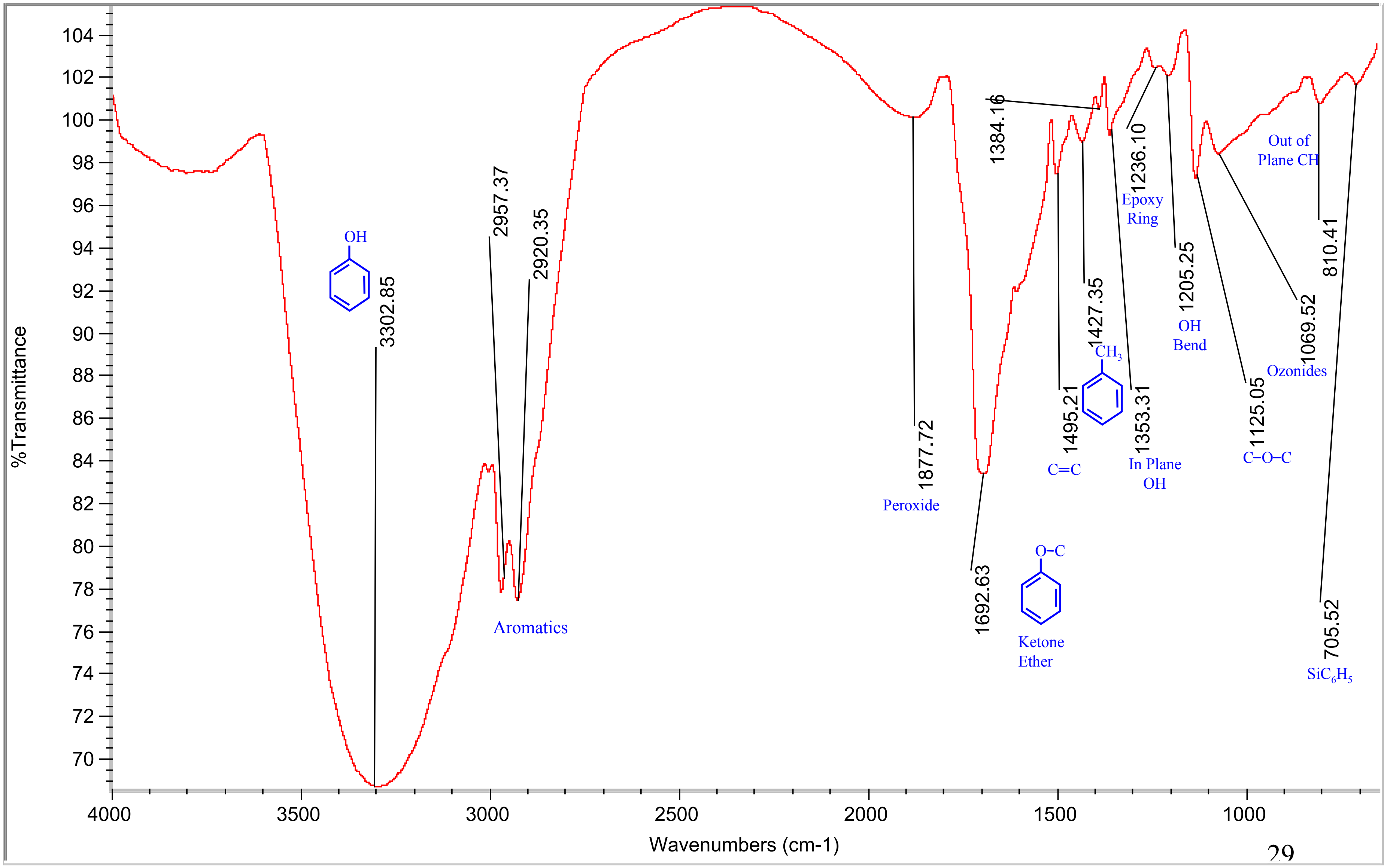
Control Wafer



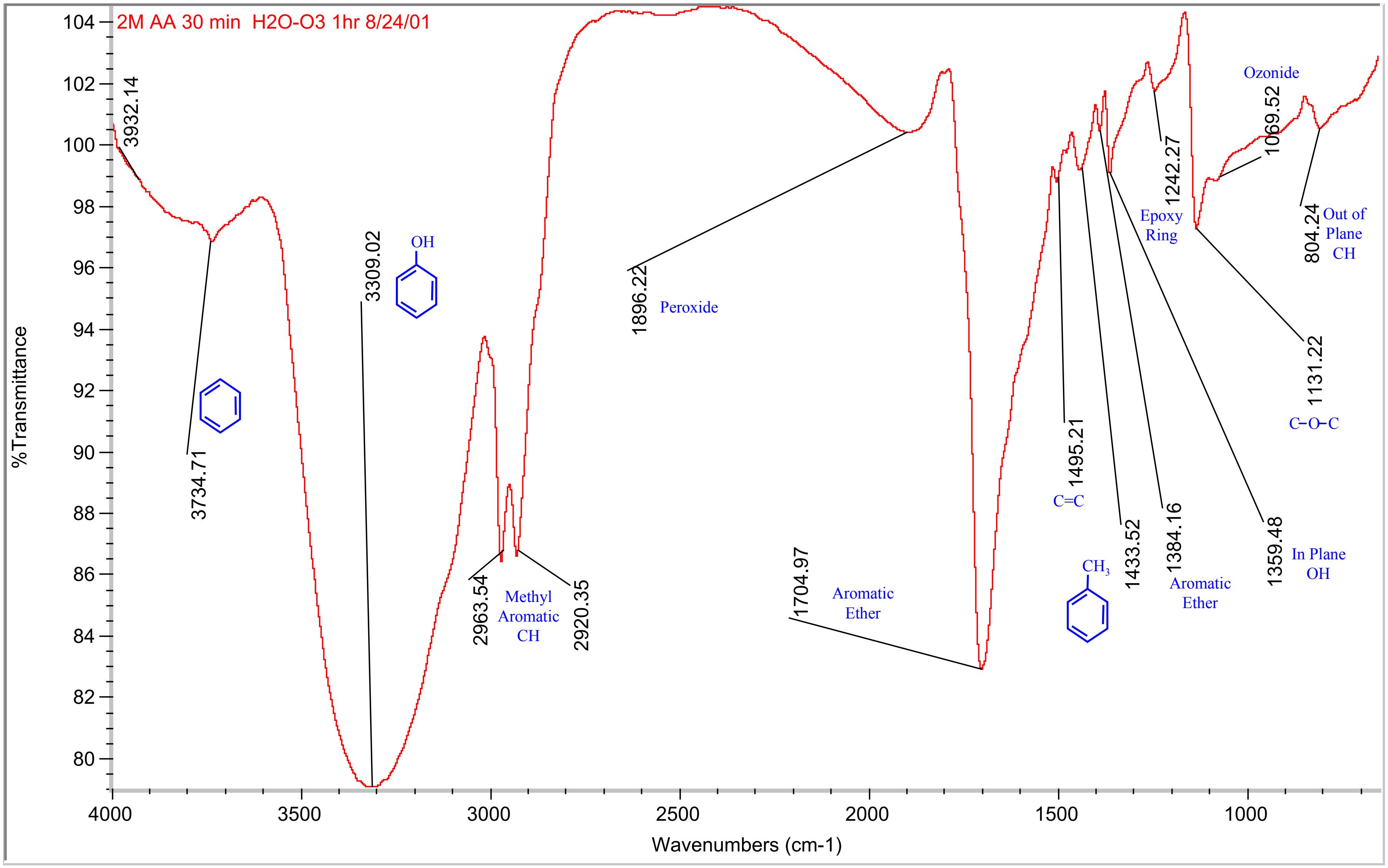
UPW/O_3 Only


a)
106
104
102
100
98
96
94
92
90
88
86
84
82
80
78
76
74
72
70
68
66
%Transmittance
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
3327.53
OH
2963.54
2920.35
Methyl CH
1199.08
OH Bend w/ CH Inplane Bend
1853.04
Peroxide
1384.16
Aromatic Ether
1711.14
Ether
1680.29
1606.26
1587.75
Ring C=C
1495.21
C=C
1433.52
1353.31
In Plane OH
1137.38
Ether
1069.52
Ozonide
804.24
Out of Plane CH
705.52
SiC6H5

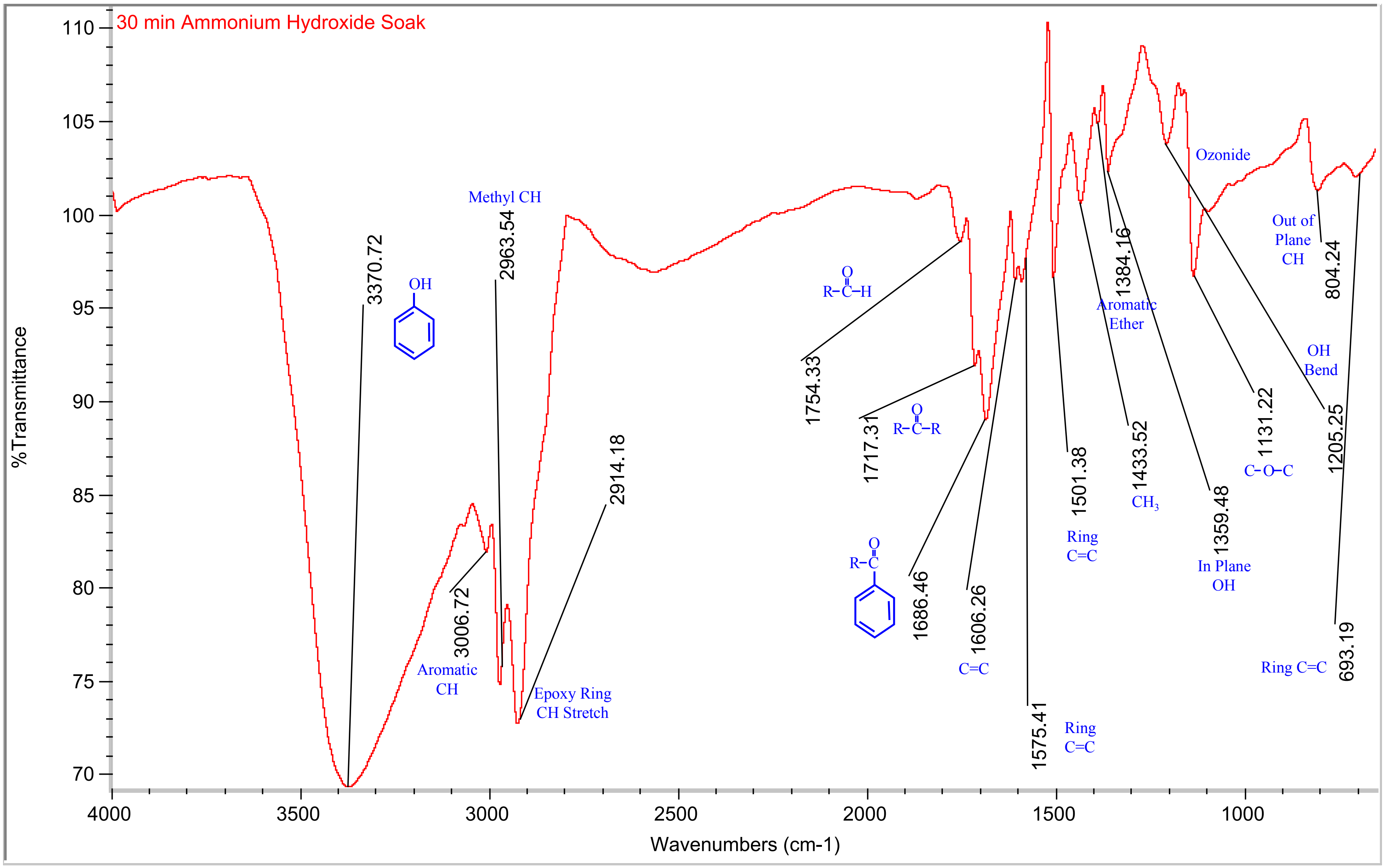
UV Wafer Pretreatment with O_3/UPW



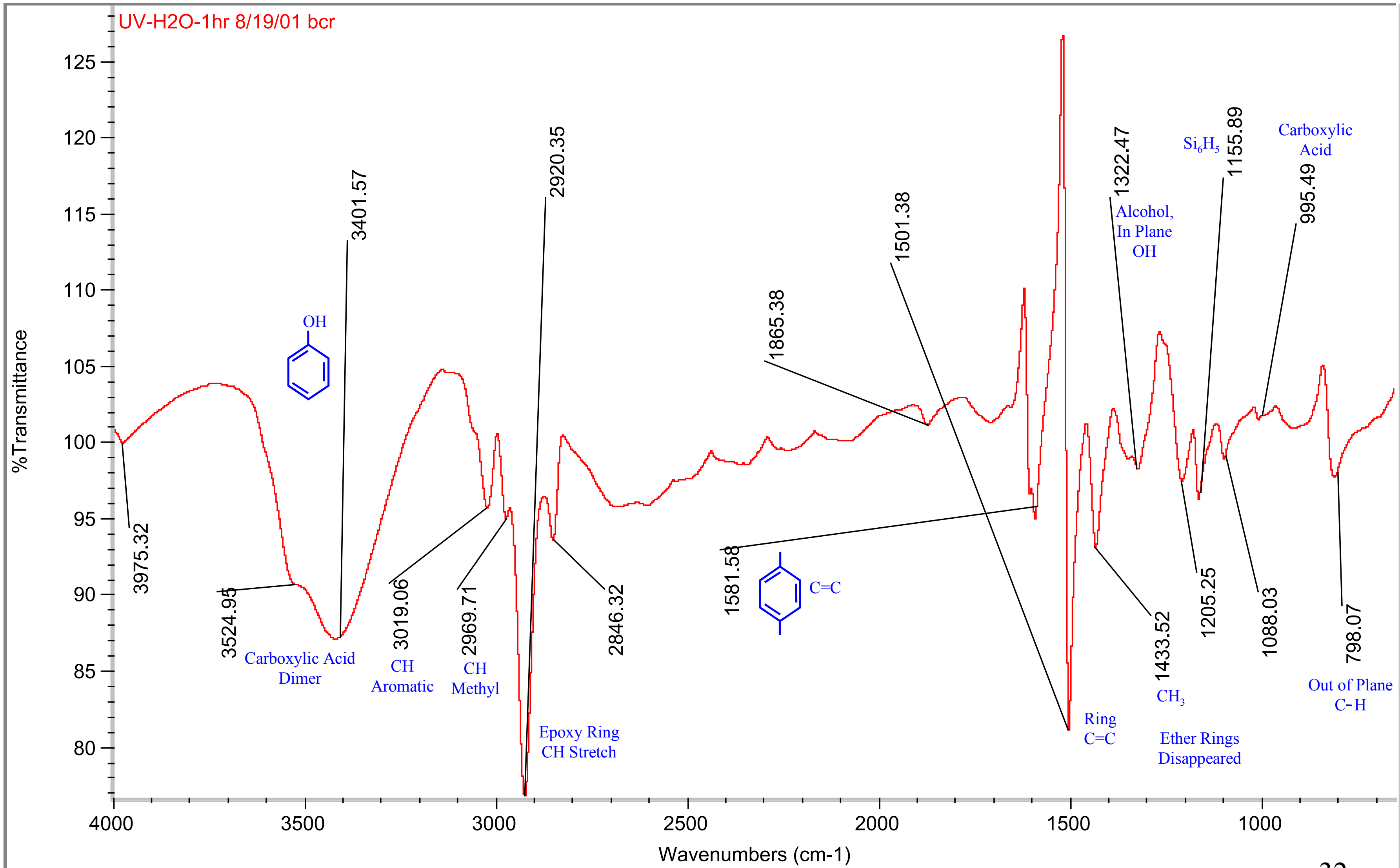
Acetic Acid Pretreatment, UPW/O_3



NH_4OH Pretreatment, UPW/O_3



UV with H_2O Only



Future Research Plans

- Fluoresce OH* radicals with Thiamine, measure with spectrophotometer.
- Follow oxidation reaction with time using FTIR to track changes.
- Coat Quartz wafers with DUV Photoresist, direct UV light thru quartz to underside of Photoresist.
- Quantify bubble effect through surface image analysis.
- Quantify oxidation via radical/ozone mechanism.

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