Thrust B

# Ozonated Water Research Directions

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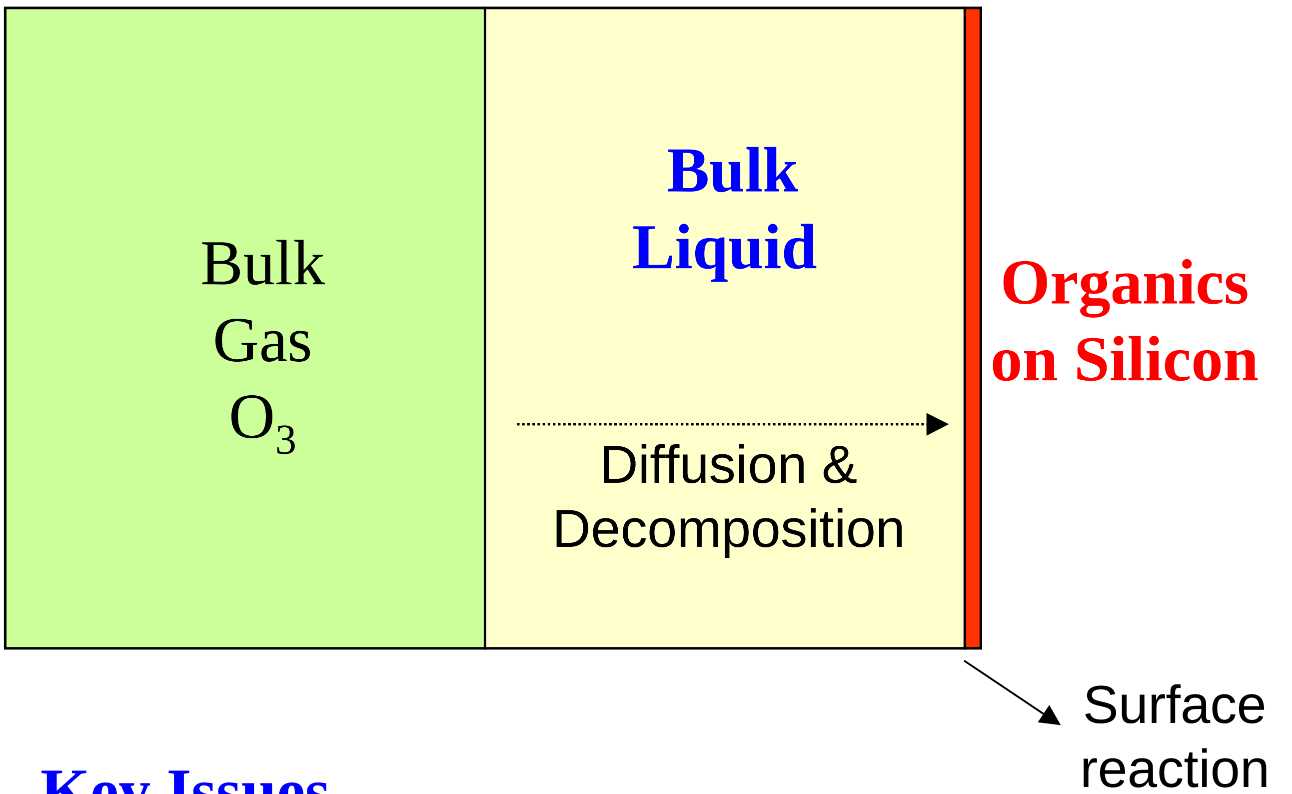
# Ozonated Water Cleaning Impact

Resist striping & replacement for Piranha cleaning

- CoO; 29% reduction compared to piranha.
- Environmental Gain
  - Eliminates most $H_2SO_4$ use and waste.
  - Less UPW use, due to elimination of $H_2SO_4$ rinse.
- Safety
  - Eliminates exposure to hot piranha
  - Need to learn how to handle $O_3$ safely.

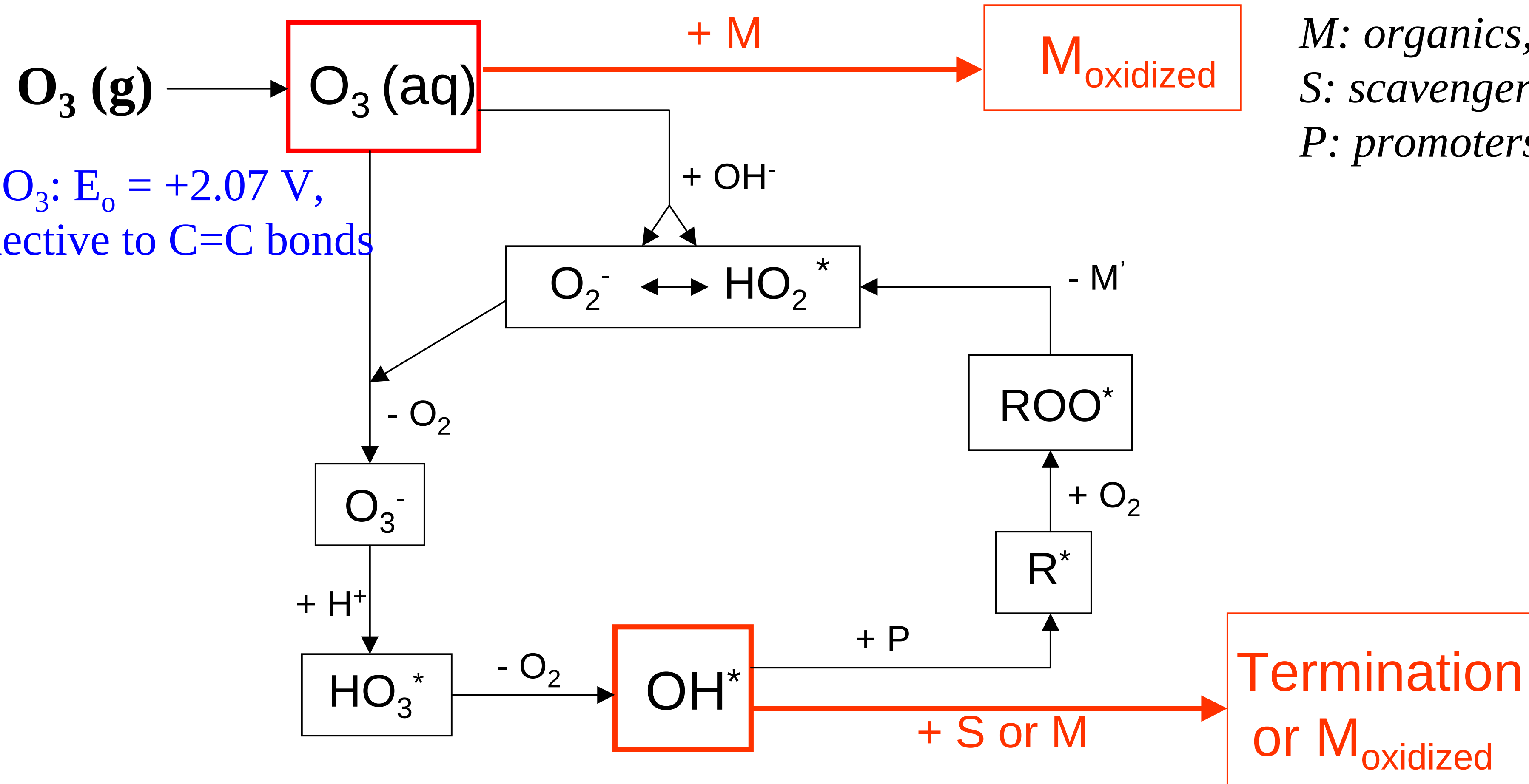
# Process




**Key Issues**

- **Boundary Layer Control**
- **$O_3$ Decomposition**

# $O_3$ Decomposition Model




*M: organics,*
*S: scavengers,*
*P: promoters*

$O_3$: $E_o$ = +2.07 V,
selective to C=C bonds

$OH^*$: $E_o$ = +3.06V, more reactive and less selective

Staehelin, et al., *Environ. Sci. Technol.* **1985**, *19*, 1206

# Chain Reaction Chemistry

1. Direct consumption of $O_3$, e.g., phenol
2. Initiation of $O_3$ decomposition, e.g., $OH^-$, glyoxylic acid
3. Propagation, e.g., formic acid, methanol

   ($OH^*$ scavenged,but $O_2^{*-}$ reformed.)
4. Termination, e.g., tert-butanol, $HCO_3^-$, $CO_3^{2-}$

   ($OH^*$ scavenged, and no $O_2^{*-}$ or $H_2O_2$ formed.)

# Cleaning Parameters

S. De Gendt et al., *Symp. on VLSI Technol. p.168, 1998.*

- pH ↑ : $[O_3]$ ↓
- promoter addition $[H_2O_2]$ ↑ : $[OH^*]$ ↑, $[O_3]$ ↓ ,
  resist removal ↓
- inhibitor addition $[CH_3COOH]$ ↑ : $[OH^*]$ ↓ , $[O_3]$ ↗ ,
  resist removal ↗
- Temperature ↑ : $[O_3]$ ↓ , but removal efficiency/$[O_3]$ ↑

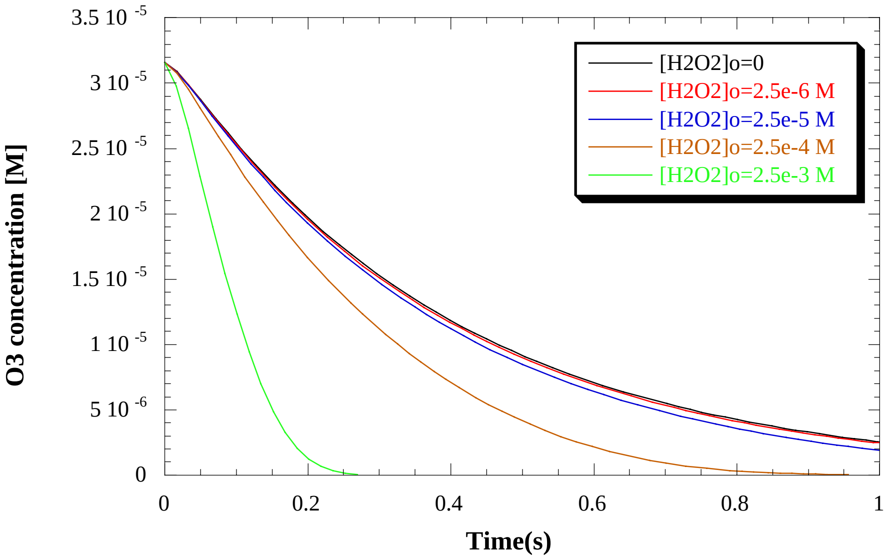
What is the chemical structure of various resists?
What are the water-soluble etch products?

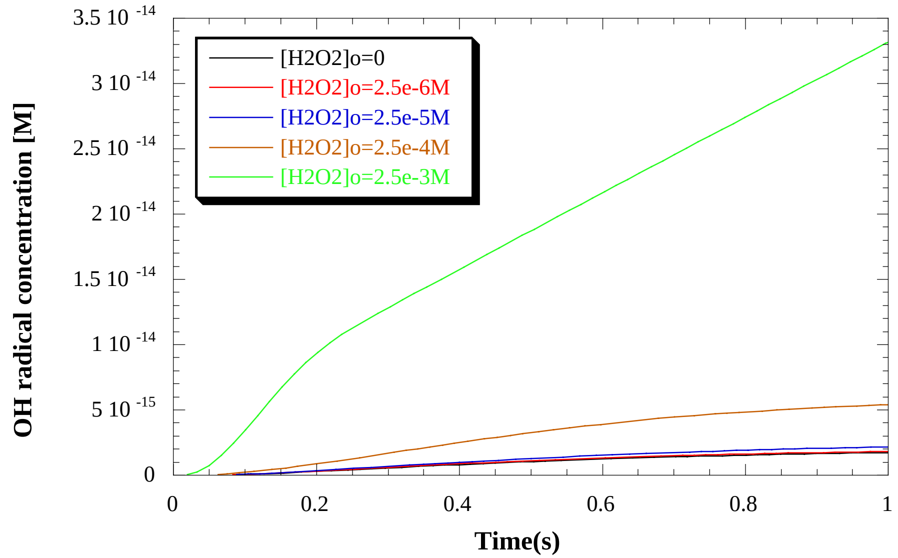
# Numerical Simulation

- Simulates direct and indirect oxidant concentrations.
- Predict the distribution of intermediate species.
- Examines the kinetic roles of scavengers and promoters on $O_3$ and $OH^*$ concentrations

# Simulation Results

$[O_3]_o = 3.16 \times 10^{-5}$ M, $[OH^-]_o = 7.17 \times 10^{-3}$ M, $[CO_3^{2-}]_o = 3.0 \times 10^{-3}$



# Some Questions

- Which oxidation is preffered, direct or indirect?
  - What is the oxidation mechanism of resist?
  - What is the main etch species, $O_3$ or $OH^*$?
- Is the decomposition model realistic?

# Future Work

- Gathering all kinetic data and Remodeling.
- Combining of simulation and experimental data.
- Elucidating $O_3$ decomposition and cleaning efficiency.
  - pH,
  - scavengers,
  - promoters…..