

*The materials integrity management company*

# Production of High Purity Functional Water at Point-of-Use for Advanced Mask Cleaning Processes

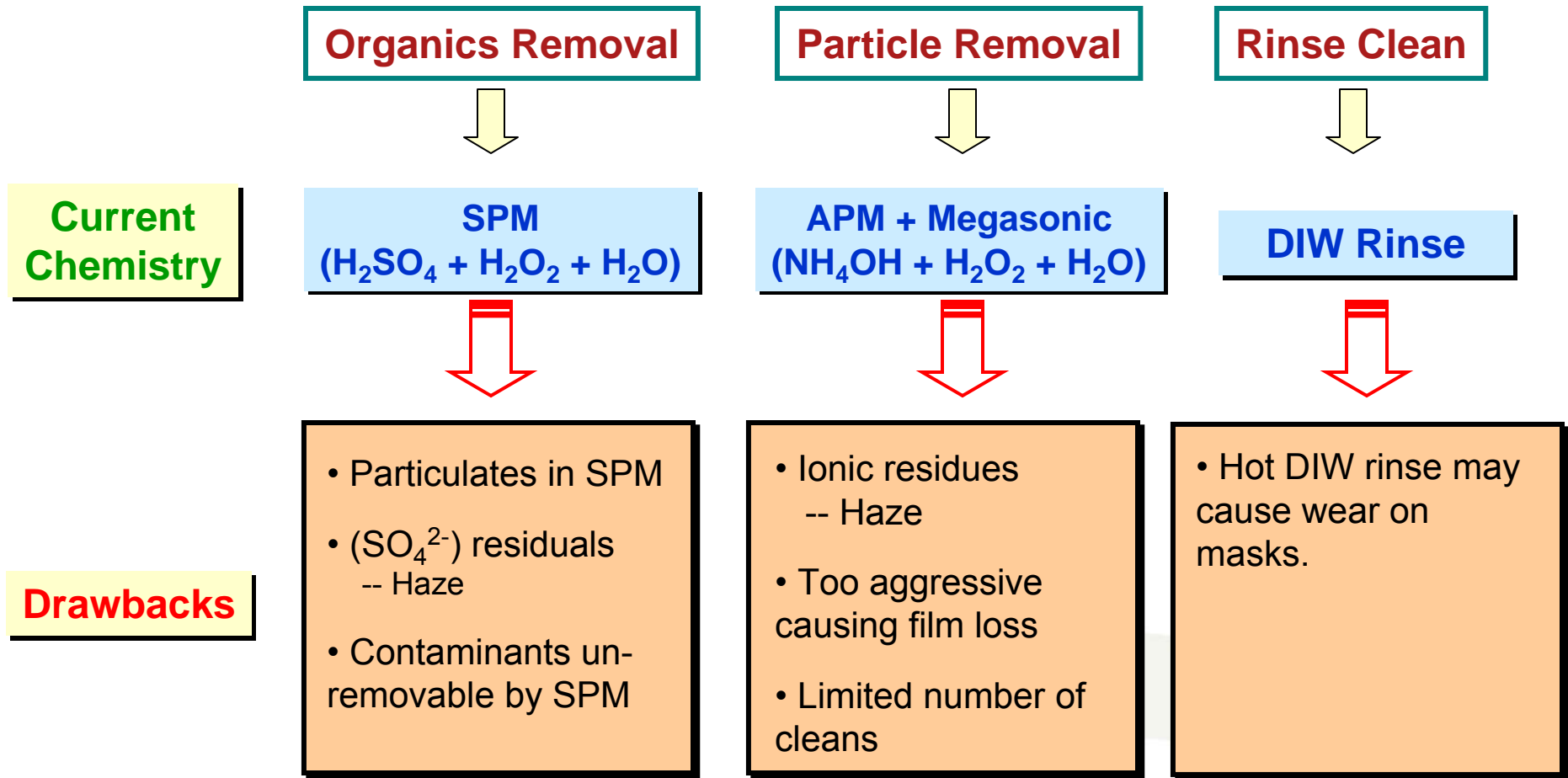
**2010 International Workshop on EUV Lithography  
June 22-24, 2010**

*Annie Xia, Sr. Applications Engineer  
Annie\_Xia@entegris.com  
Entegris Inc.*

## Abstract

- Without the use of traditional pellicles, EUV masks demand high purity and effective but mild cleaning techniques for protection from defects. Recently, trends towards dilute chemistries and progress in megasonic cleaning have brought renewed interest in gasified DI water.
- In this paper, we describe the design and development of a point-of-use functional water treatment system, specifically for advanced mask cleaning applications. The system is comprised of two modules – the purification module and the gasification module. The purification module provides treatment features including TOC reduction, sub-micron particle retention, as well as thermal and pressure control. The gasification module is capable of delivering bubble-free DI water with various gases (O<sub>3</sub>, N<sub>2</sub>, H<sub>2</sub>, CO<sub>2</sub>, NH<sub>3</sub>, etc.) over a wide concentration range. The gasification module is also equipped with automatic dissolved gas concentration control feature to allow precise control and minimal process variations.

# Limitations of Sulfur-based Wet Cleaning Process



**Current cleaning processes do not provide mask surfaces that are free from contamination. → Adders!**

# Definition of Functional Water



Pure Water

+

## *Physical / Chemical Processing*

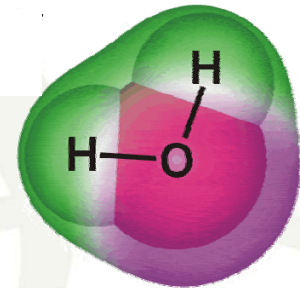
- Electrolysis
- Gasification
- Chemical Addition
- Light Irradiation
- Ultrasonic Excitation
- ...

||

## *Functional Water:*

Altered physical / chemical properties:

- Dielectric constant
- Viscous force
- Electrical conductivity
- Surface tension
- Oxidation-reduction potential



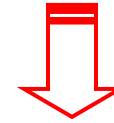
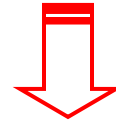
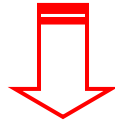
Enhanced  
Cleaning Efficiency!

# Sulfur-free Cleaning using Functional Water

Organics Removal

Particle Removal

Rinse Clean



New  
Chemistry

O<sub>3</sub> / DI Water  
( 5 – 50 ppm)

H<sub>2</sub> / DI Water  
+ Megasonic  
( < 3 ppm)

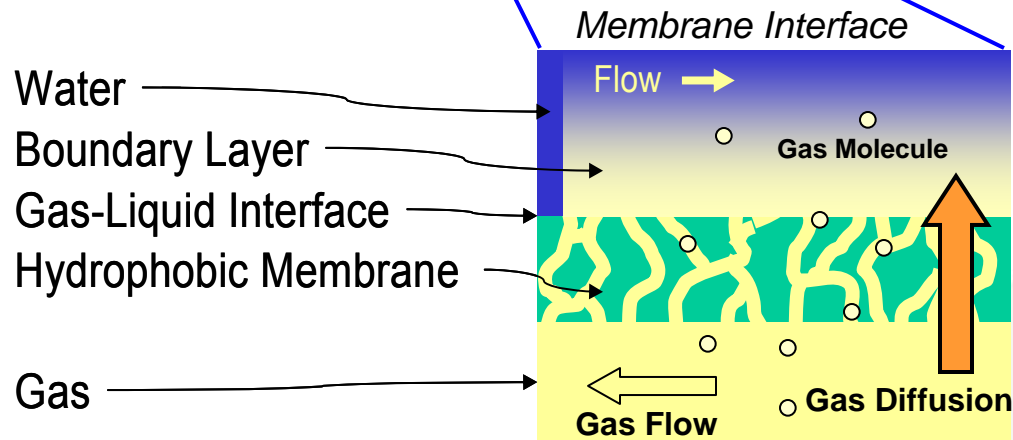
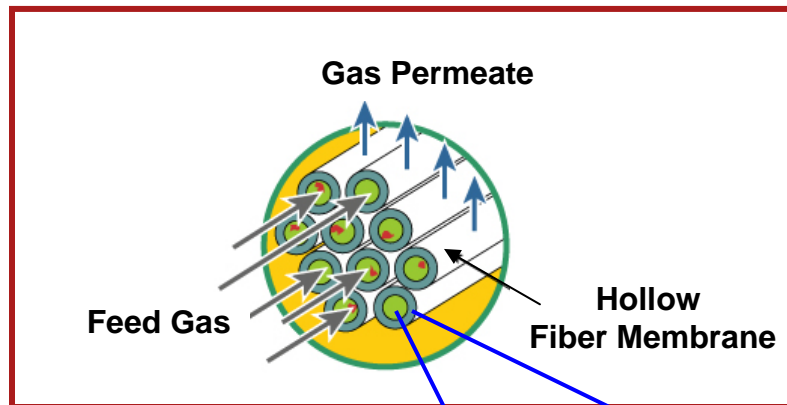
DI Water Rinse  
CO<sub>2</sub> / DI Water (Optional)

## Advantages of Functional Water

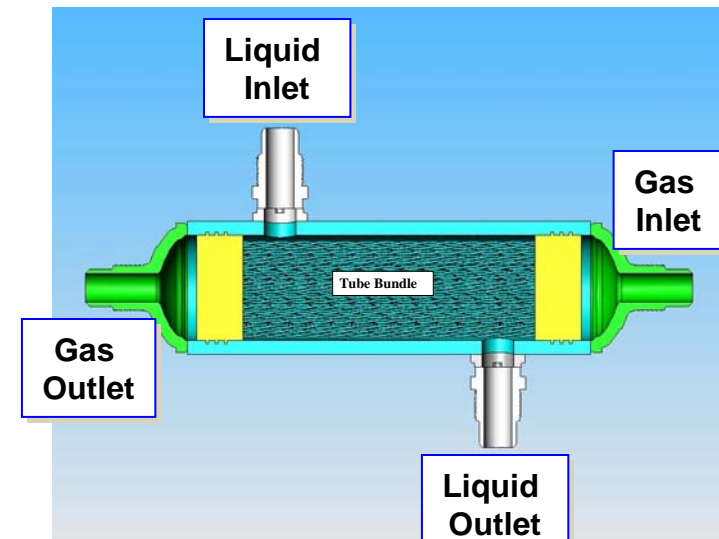
- \* Made at point-of-use
- \* Cleaner than SPM
- \* No waste except H<sub>2</sub>O and gas
- \* Relatively low cost
- \* Good cleaning efficiency
- \* Compatible with existing tools
- \* Environmentally friendly
- \* Can be room temperature

# Liquid Gasification using Membrane Contactor

## Hollow Fiber Membrane

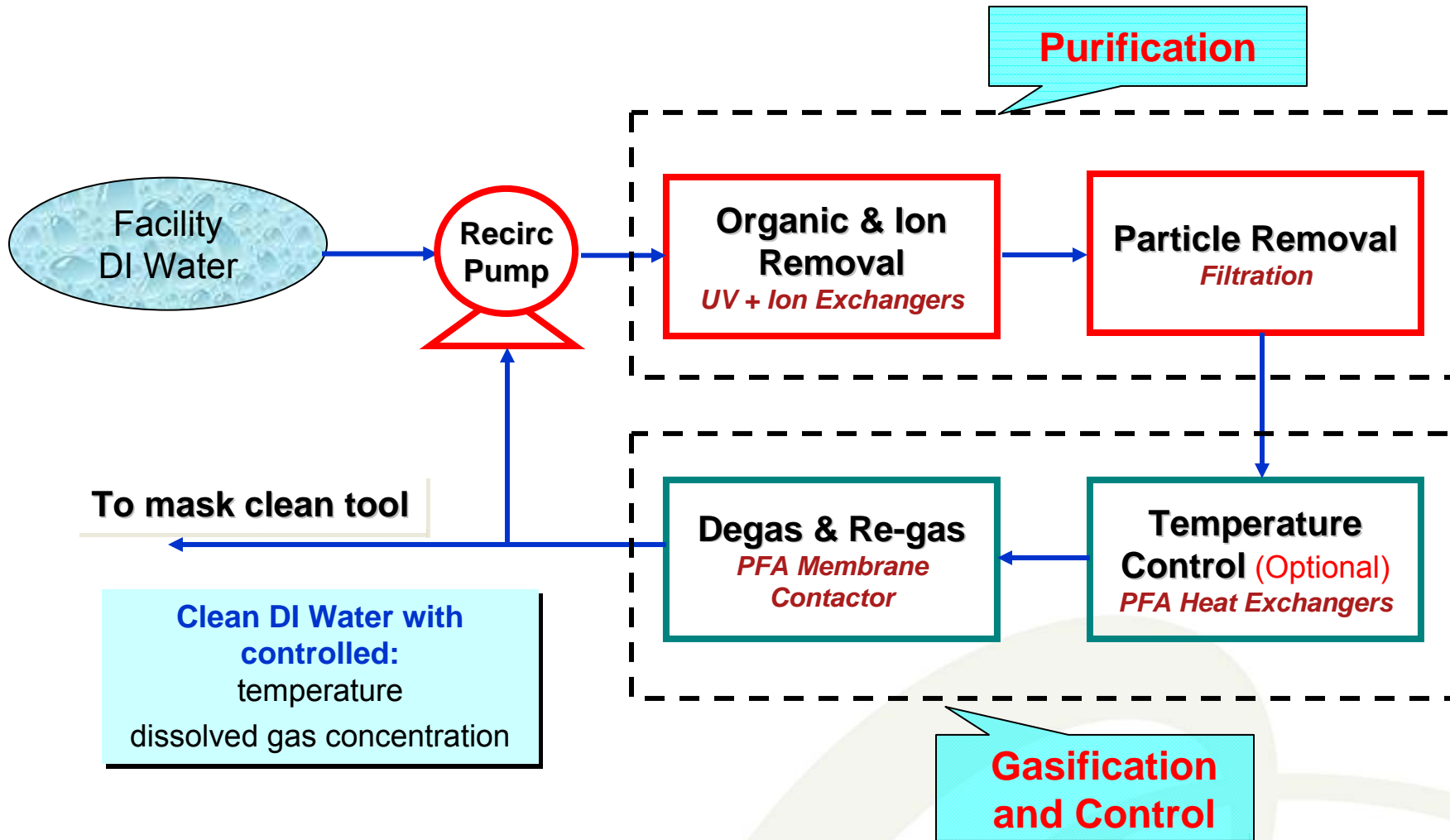


## All PFA Membrane Contactor



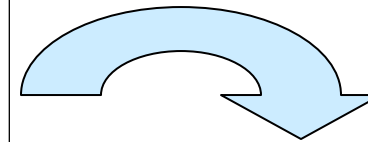
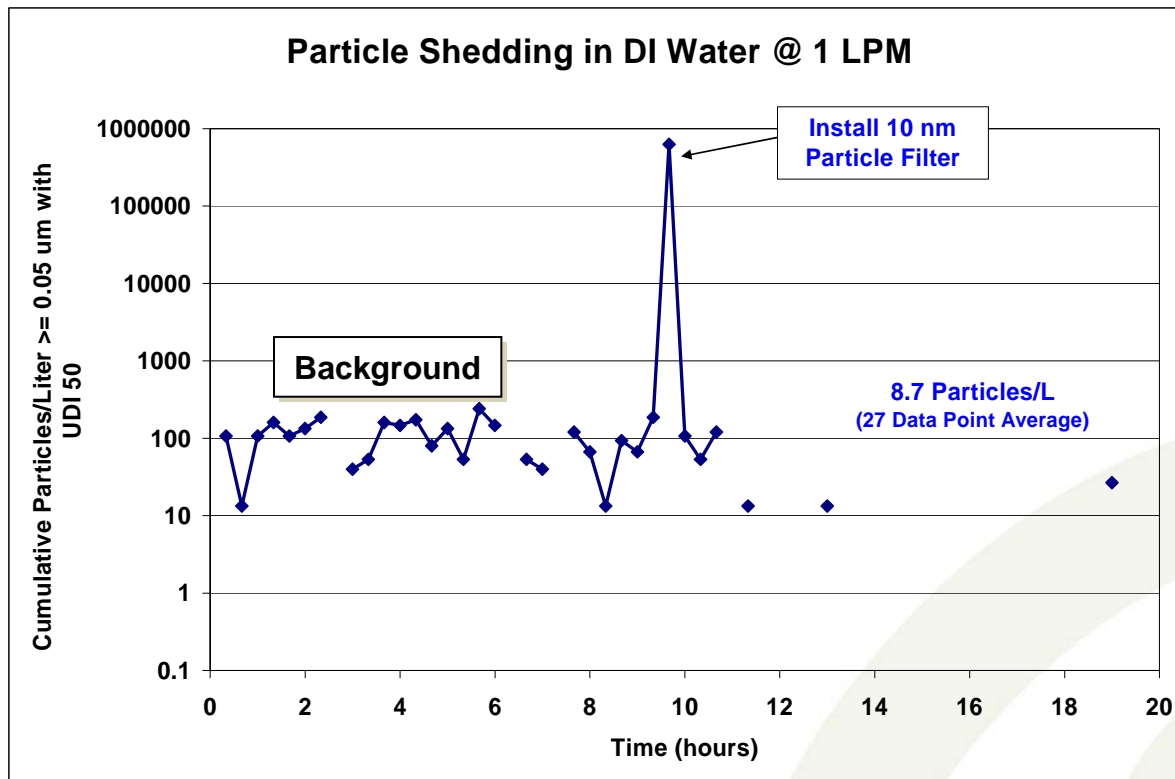
- **All PFA ultra-clean construction**
  - Low extractable and particles
  - Excellent chemical compatibility
- **PFA hollow fiber membrane**
  - Only gas permeable, Hydrophobic
  - 2 m<sup>2</sup> membrane surface
- **Low pressure drop**
  - < 7 kPa @ 8 Liter/min water flow

# Concept of Point-of-Use Ultra-pure Functional Water Polishing and Gasification System



# Typical Ionic Purification and Particle Removal

- Typical outlet DI water contains PPQ levels of ionic species:
  - Less than 0.5 ppt / each element
    - (Li, Na, Mg, Al, K, Ca, Ti, Cr, Fe, Mn, Ni, Cu, ...)
- Typical outlet DI water contains single digit particles per liter.

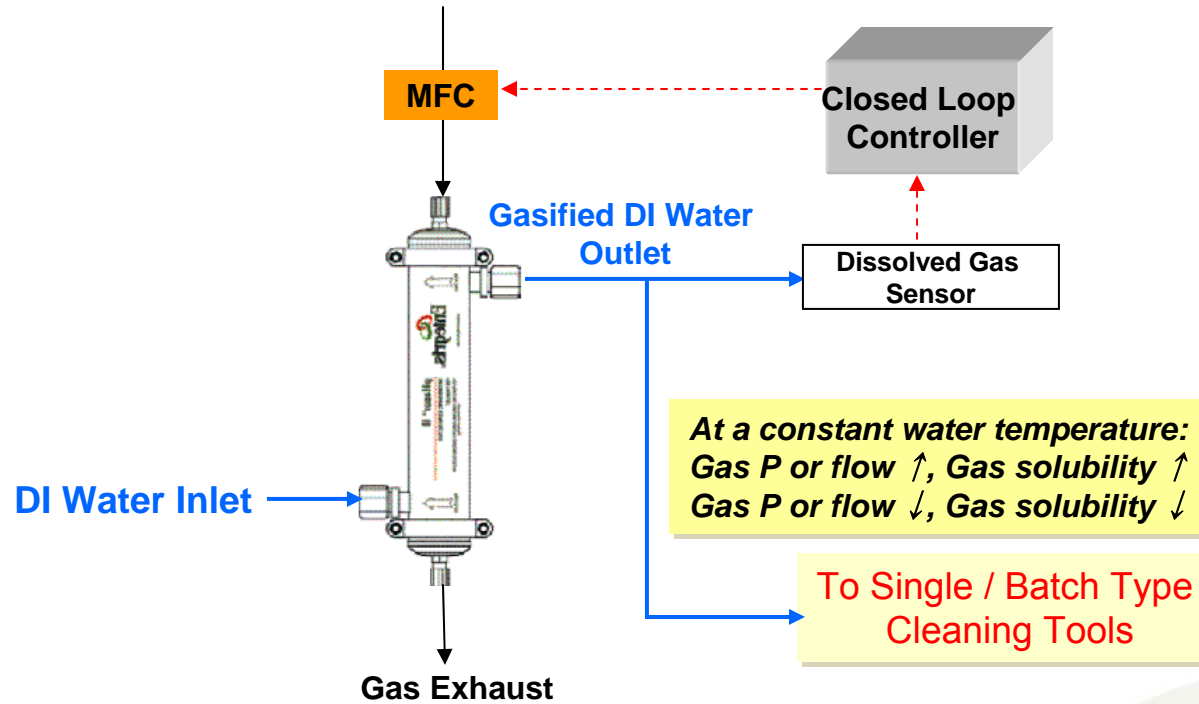


Outlet DI water Particles  
< 10 counts / Liter ( $> 0.05 \mu\text{m}$ )



# Automated DI Water Gasification Process

*Degas & Regas in one step*



## Types of Dissolved Gas Sensors

- O3-DIW:**
  - Dissolved O<sub>3</sub> sensor
  - ORP sensor
- H2-DIW:**
  - Dissolved H<sub>2</sub> sensor
  - ORP sensor
- N2-DIW:**
  - Dissolved N<sub>2</sub> sensor
- CO2-DIW:**
  - Dissolved CO<sub>2</sub> sensor
  - pH meter
  - Resistivity sensor

ORP – Oxidation Reduction Potential

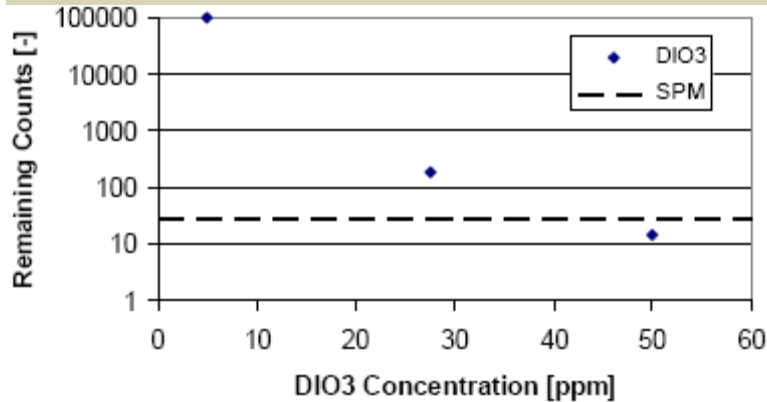
### *How does the control system work:*

- Dissolved gas sensor sends feedback to closed loop controller.
- Closed loop controller keeps adjusting gas flow until dissolved gas sensor measurement matches the setpoint.

Direct Gas Injection!  
 No Gas or Liquid Mixing!

# Why do we need to control gas concentration?

**O3 Concentration vs. Cleaning Efficiency**



O<sub>3</sub> concentration affects cleaning efficiency!

Maintaining stable O<sub>3</sub> concentration

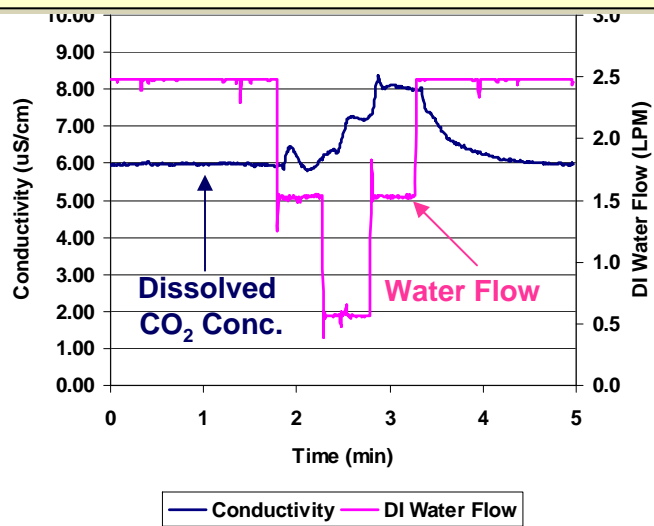


Consistent cleaning efficiency

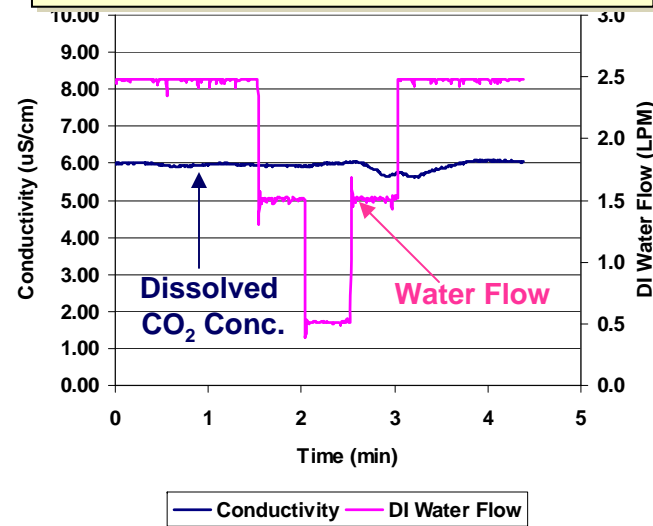
Source: Investigation of Sulfur Free Clean Processes for Next Generation Lithography. C. Chovino, et al, AMTC GmbH

Auto concentration control minimizes process variability!

**Without Auto Concentration Control**

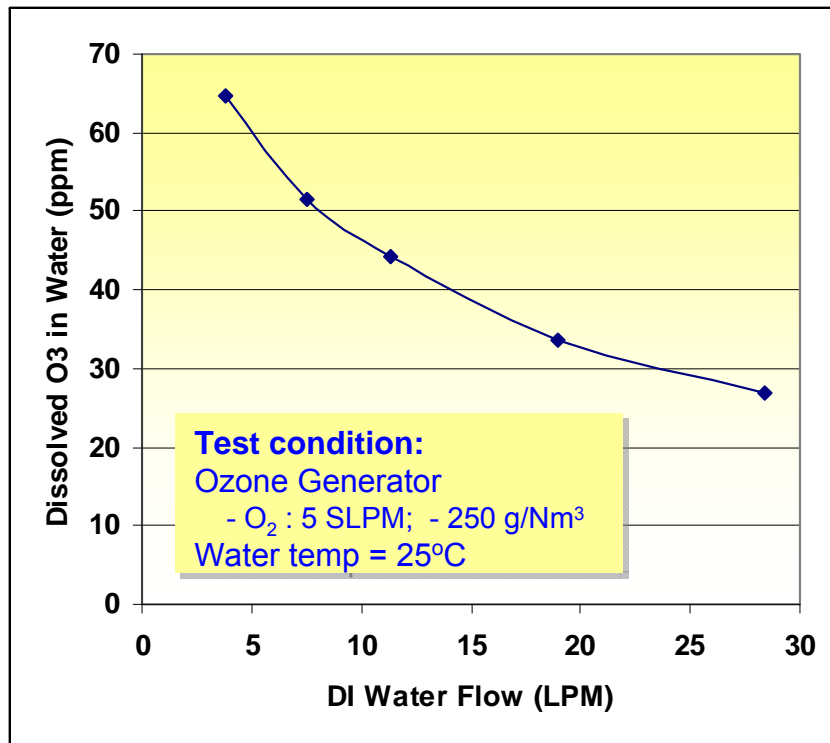


**With Auto Concentration Control**

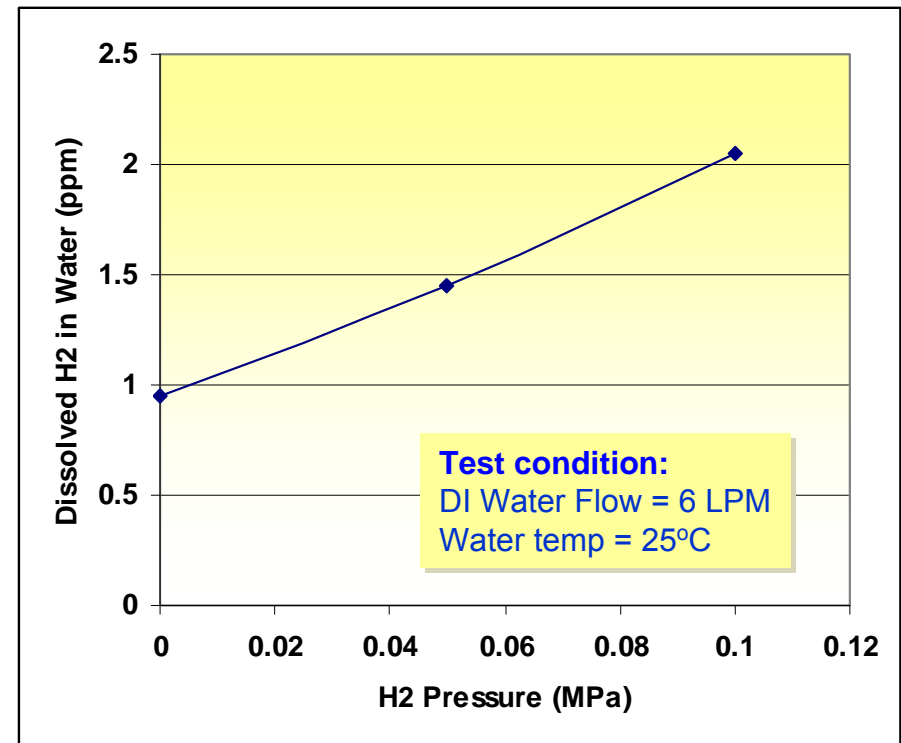


# Water Ozonation and Hydrogenation Efficiency

**Dissolved O<sub>3</sub> Concentration vs. Water Flow**  
(Single Membrane Contactor)



**Dissolved H<sub>2</sub> Concentration vs. H<sub>2</sub> Pressure**  
(Single Membrane Contactor)



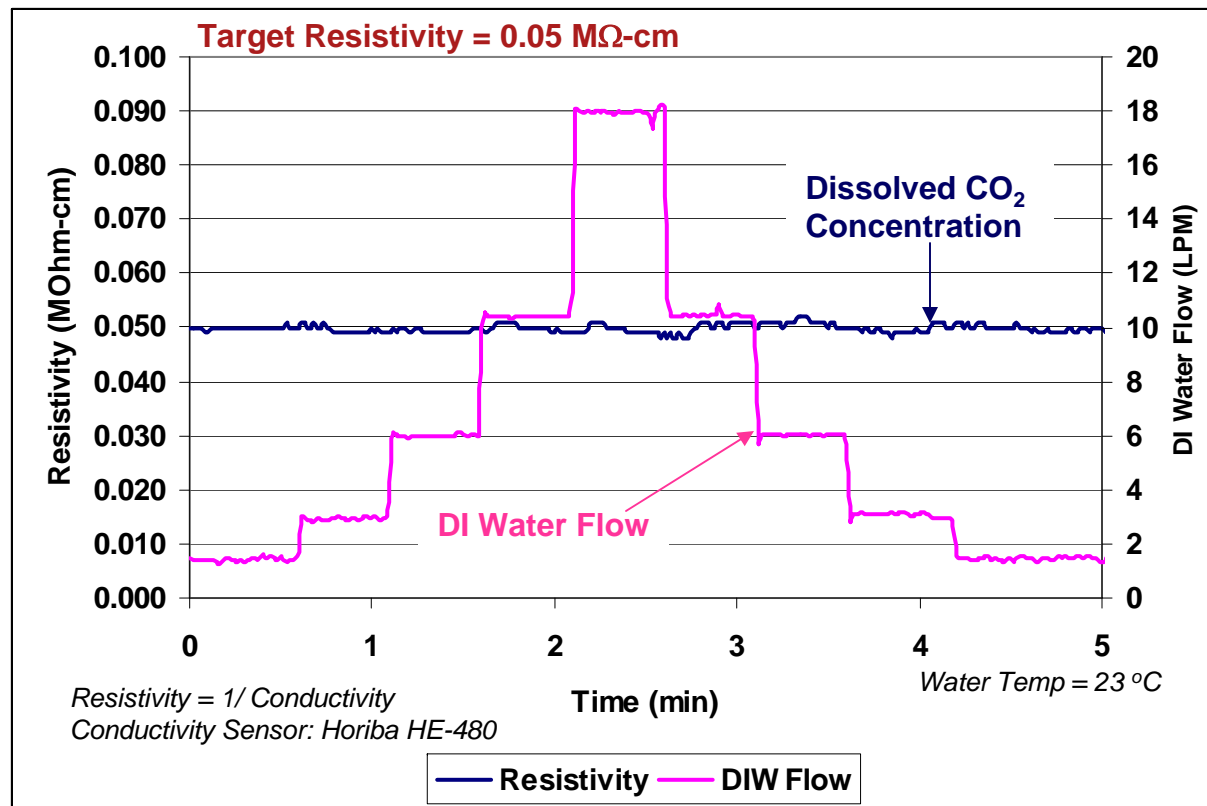
- To adjust dissolved O<sub>3</sub> concentrations:
  - Inlet O<sub>3</sub> concentration ↑, Dissolved O<sub>3</sub> concentration ↑; vice versa
  - Inlet O<sub>2</sub> flow ↑, Dissolved O<sub>3</sub> concentration ↑; vice versa

- To adjust dissolved H<sub>2</sub> concentration at a given flow:
  - H<sub>2</sub> pressure ↑, Dissolved H<sub>2</sub> concentration ↑; vice versa

# Gasification System Control Performance

1.5 → 3 → 6 → 10.5 → 18 → 10.5 → 6 → 3 → 1.5 LPM (every 30 seconds)

Dissolved  $\text{CO}_2$  concentration (Water Resistivity) stability within  $\pm 5\%$  of Setpoint!



# Summary

- A point of use functional water delivery system using membrane contacting technology enables:
  - Purification and filtration at point-of-use
  - Precise control at point-of-use
  - Less chance of contamination at point-of-use
- Automatic control of dissolved gas concentration brings added benefit of ensuring a stable and seamless cleaning process.