

Towards Sustainable Fab: Reducing Bulk Chemicals by SPM Reuse in Single-Wafer Process Applications

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SCREEN: Innovation Inspired by Sustainability
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Agenda

◆ Background

- Use of Sulfuric Peroxide Mixture, SPM
- Growth

◆ Approaches

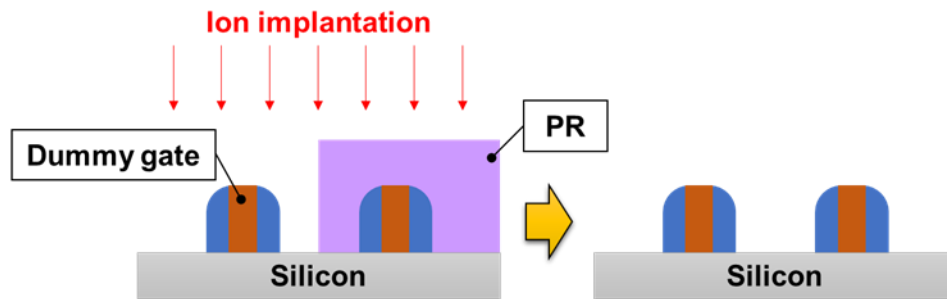
- SPM Reuse
- SPM Replacement

◆ Conclusion

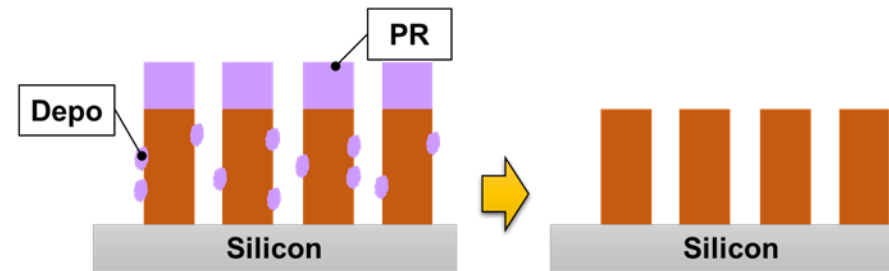
H₂SO₄, Sulfuric Acid

- ◆ SPM, sulfuric peroxide mixture, is used primarily for the removal of organic materials, e.g. photoresist, etch residues, from silicon wafers.

I/I resist removal



Post Dry etch cleaning



- ◆ One of the most widely used chemicals in the fab.
- ◆ SPM has a large impact on the cost of chemicals and environmental aspects.
- ◆ Annual consumption is expected to increase due to increase in the number of processing steps and demand for electronic devices worldwide.
- ◆ The global electronic grade sulfuric acid market size was assessed to be \$305M in 2021 and projected to reach \$415M by 2026.

Drivers to Reduce H_2SO_4



- ◆ Chemical cost reduction
- ◆ Facilities forced to migrate from totes to bulk isotainers
 - Increases upfront infrastructure costs
- ◆ H_2SO_4 constitutes 90% of facility acid load
 - Needs to be neutralized
 - No longer can discharge neutralized brine to sewer water since exceeds discharge limit
 - Requires expensive brine management system
 - Brine concentrator evaporators and crystallizers needed
- ◆ H_2SO_4 reuse can reduce size or eliminate brine mgmt. system

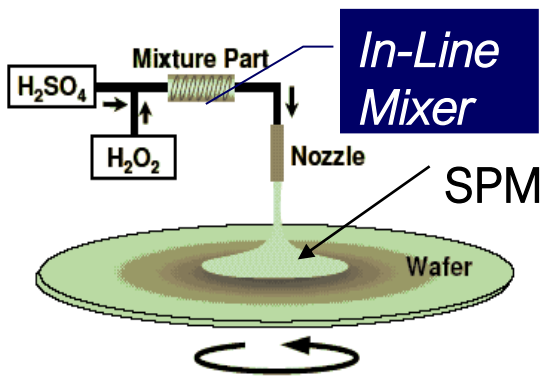
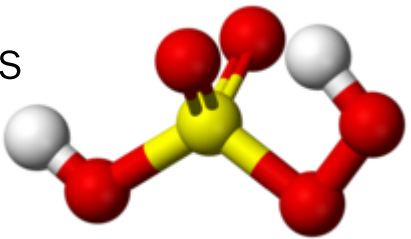
1 <https://www.chemworld.com/Sulfuric-Acid-NSF-approved-p/66be-4200.htm>

2 <http://hwfttech.com/standard-tank-container.html>

Trend of SPM process transfer from batch to single

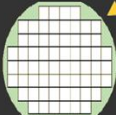
◆ Feature : Advantage of Single-wafer SPM

- Single-wafer SPM, which mixes chemical just before dispense, contains a large concentration of Caro's acid and increase removal ability.
- Superior particle performance due to fresh SPM supply.
- Superior process performance due to lower boundary layer.



ISSM, 2005
Novel Photo Resist Stripping for Single Wafer Environmentally Friendly Process

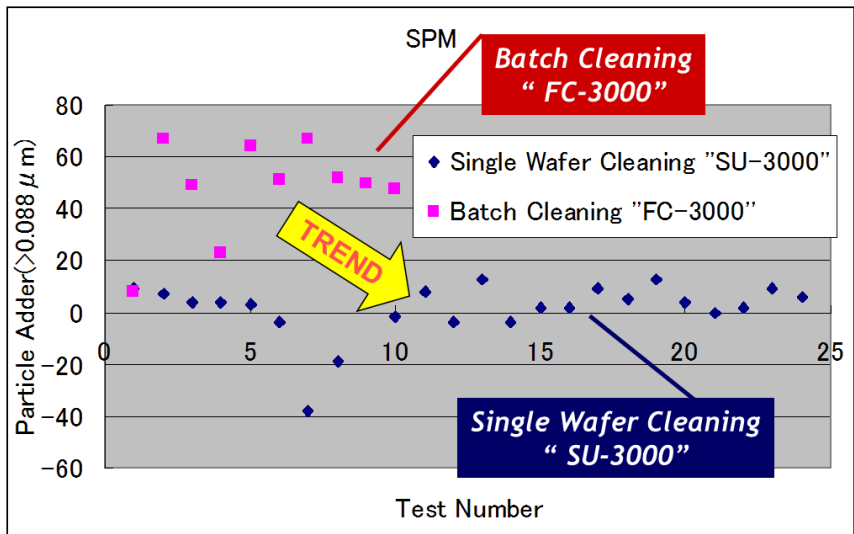
Single SPM				Batch SPM					
SHARK				従来技術 (SPM)					
		Dose量					Dose量		
		1E13	1E14	1E15			1E13	1E14	1E15
Ion種	B	○	○	○	Ion種	B	○	○	○
	BF	○	○	○		BF	○	○	○
	Ge	○	○	○		Ge	○	○	×
	P	○	○	○		P	○	○	×
	As	○	○	○		As	○	○	×



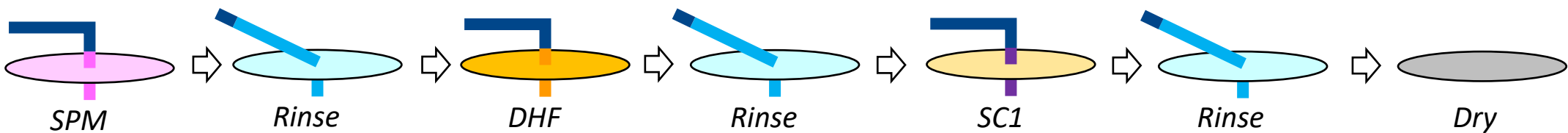




2005 Japan Society of Applied Physics
Atsushi Okuyama, Itsuro Ishizaki, Hayato Iwamoto, *Akio Hashizume
Sony Corporation, *DAINIPPON SCREEN MFG.CO.,LTD



- Multiple chemical sequences are possible in same chamber



SPM Reuse

H₂SO₄ Conc Decay over Time

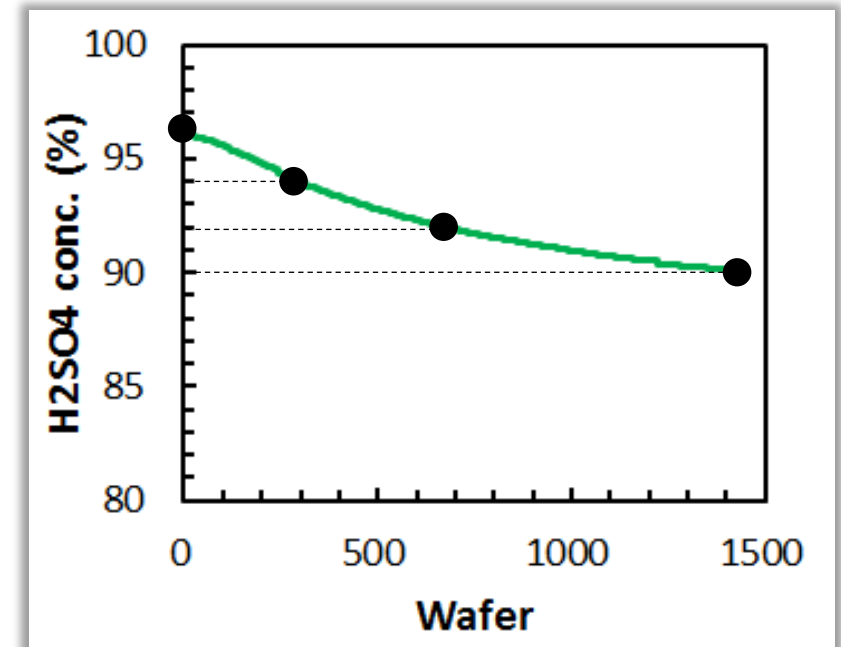
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As H₂SO₄ conc. decays through use, the time to strip increases.



SPM Reuse System

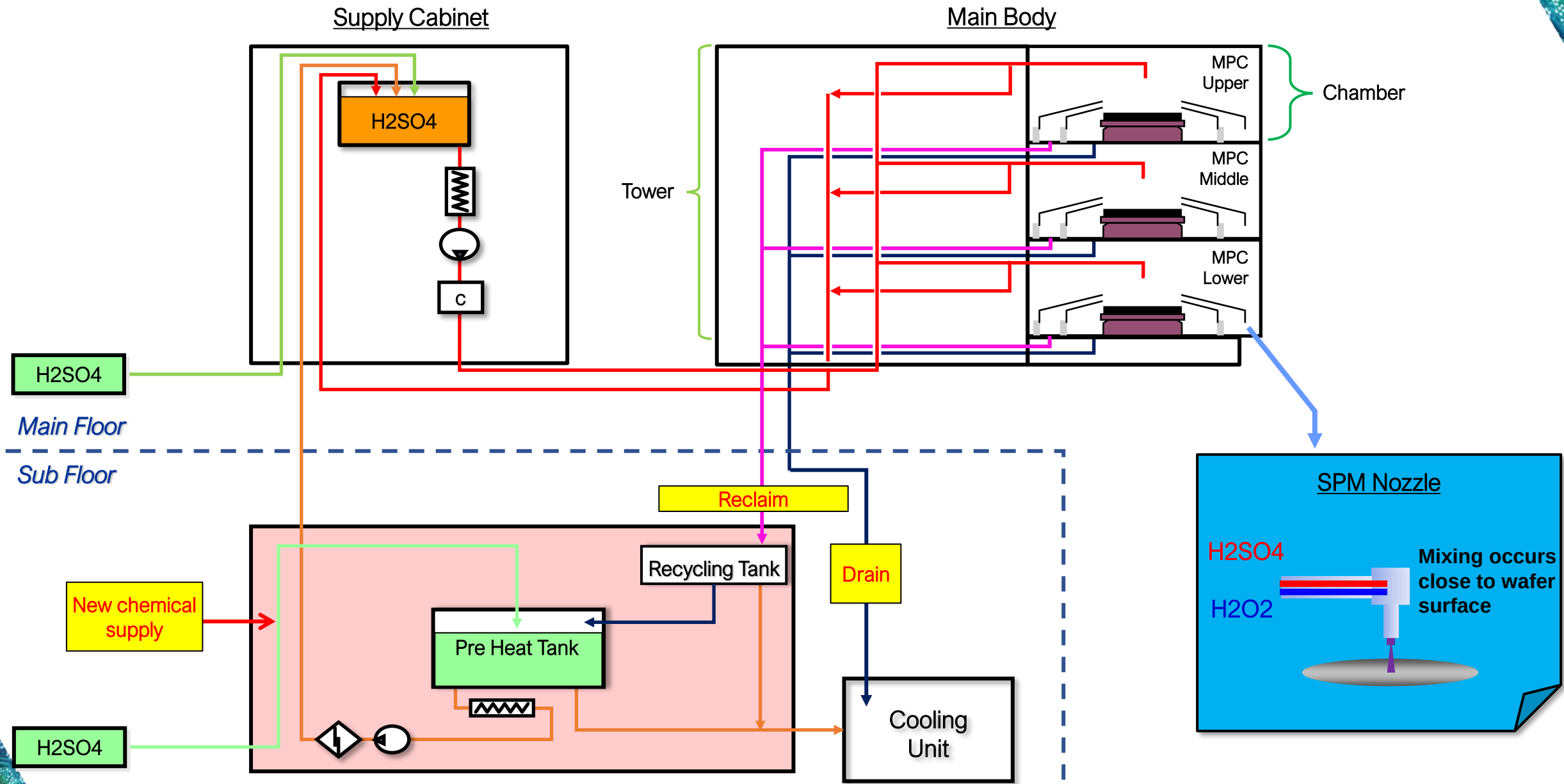
Total of 18 chambers



Per 1500 wafer PR stripping process,
H₂SO₄ conc. decays by approximately 5%

Single Wafer Cleaner SU-3300

SPM Reuse Schematic



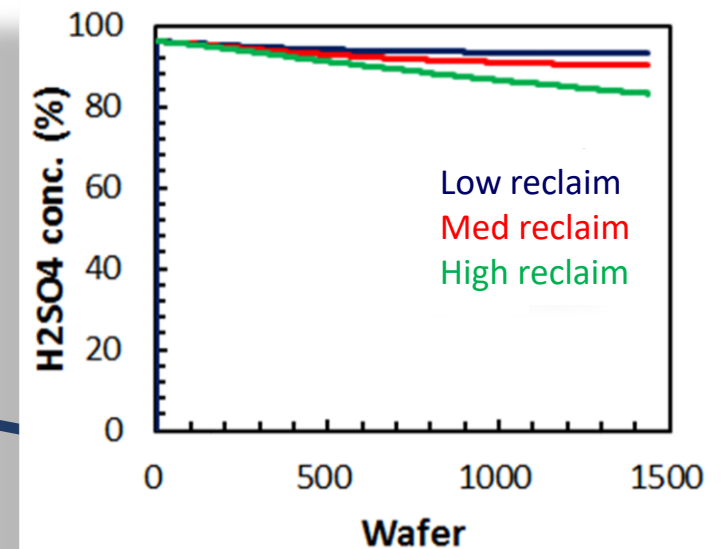
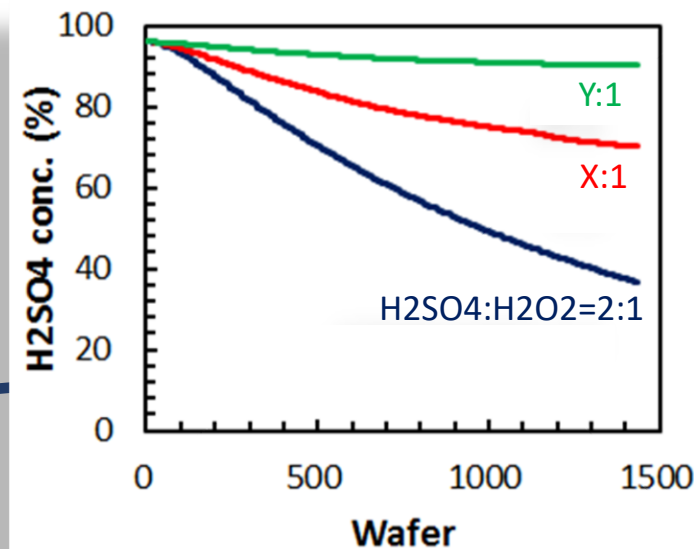
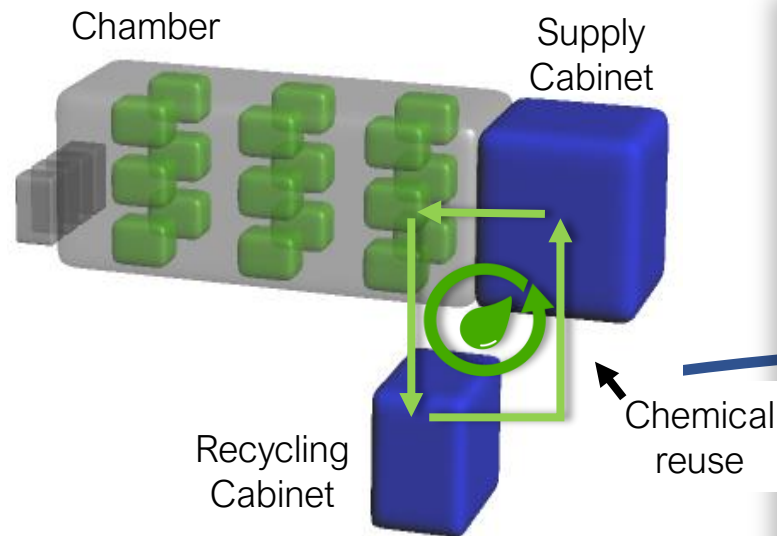
Determination of SPM Reuse Ratio & Reclaim %

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Using data from the SPM reuse system, we calculated the chemical consumption rate

H₂SO₄ Dilution Data

Simulation based on a single chamber cycle



Different solution ratio

Different reclaim %

SPM Reduction via SPM Reuse

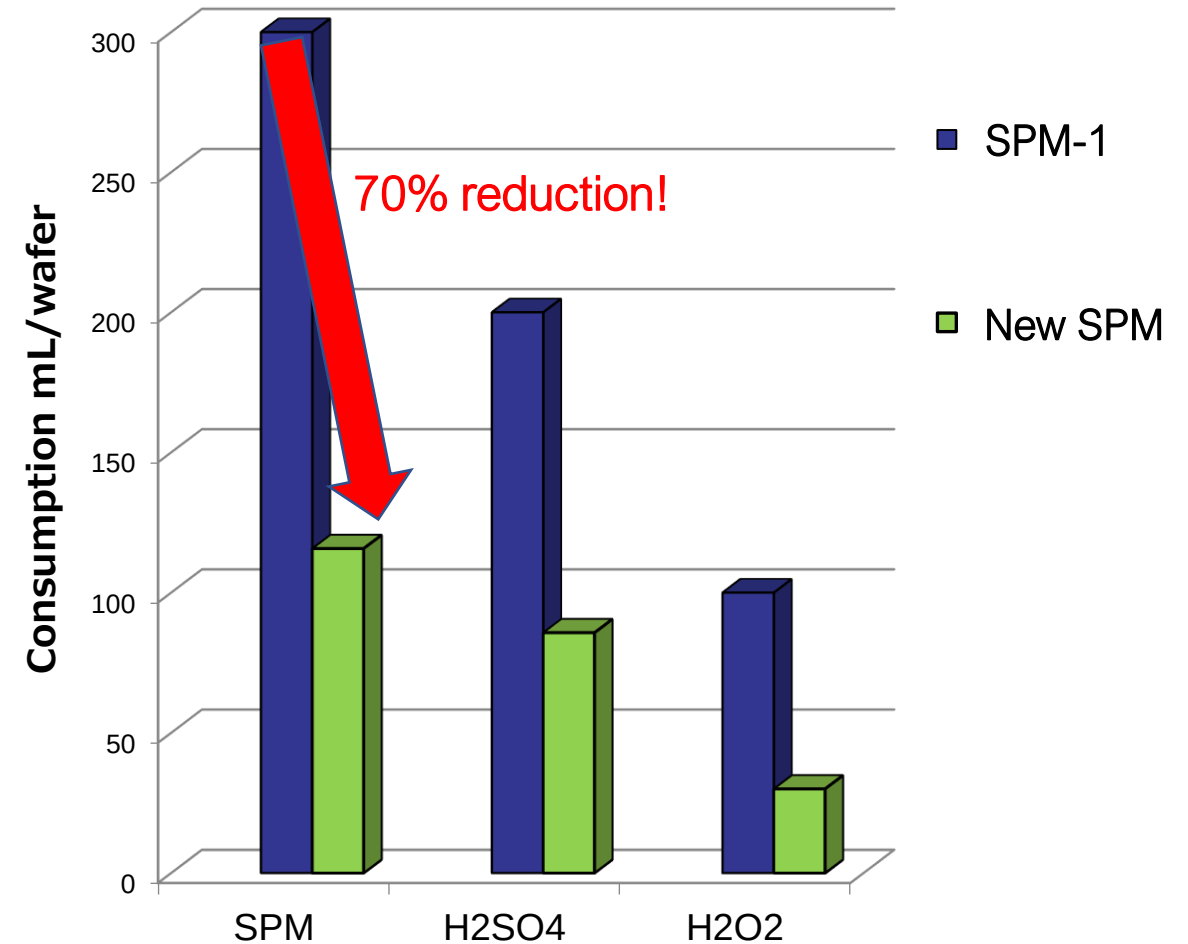
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Chemical consumption data

Test Conditions

1. SPM-1/No reclaim
SPM mixing ratio : 2:1, 30sec

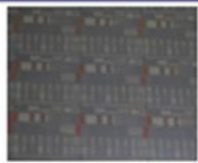
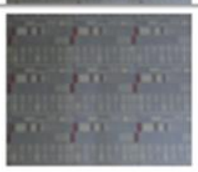
2. New SPM
SPM mixing ratio : Y:1, 30sec
With Reclaim



Resist Removal Performance Results



Resist removal of **New SPM** using H_2SO_4 conc. of **90%** and higher (with reclaim)
yielded indiscernible results as the removal rate of **SPM-1** (POR) using H_2SO_4 conc. of **96%**.

		New SPM					SPM-1
		H2SO4 conc.	96%	94%	92%	90%	96%
SPM Time	40s						
	60s						
	100s						
	130s						
	140s						



SPM Replacement

Investigation of SPM Replacement with Other Chemistries

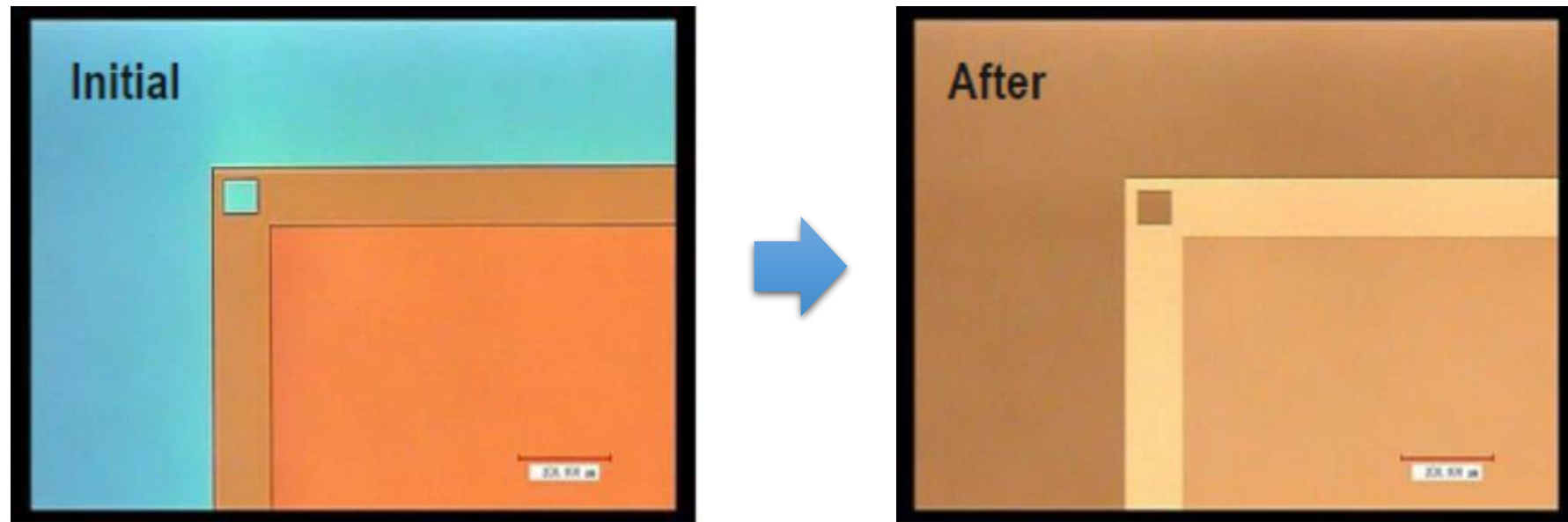
Focus on chemistry with high Oxidation-Reduction Potential (ORP)

Oxidant	Reaction	ORP (V)
Oxygen radical	$O + 2H^+ + 2e^- \rightarrow H_2O$	2.42
Ozone	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.07
Persulfate ion (SPM)	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	2.01

Ozone water is unable to strip high-dose implanted PR

Oxygen radical generated by thermal decomposition of ozone has high ORP

Removal Performance of Oxygen Radical for I/I Photoresist



Sample: KrF Resist, 350 nm

Doping Condition: As, 1E15

PR was completely removed as shown by microscope and ellipsometry

Conclusions

- ◆ Migration from batch to single-wafer SPM process done due to improved process performance and defectivity improvement.
- ◆ SPM reuse on single-wafer tool can provide equivalent process performance as single-pass dispense with 70% reduction in SPM.
- ◆ Replacement of SPM with oxygen radical shows promise in removal of ion implanted photoresist and potential for SPM-free process.

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