Development of an All-Wet Benign Process for Stripping of Implanted State-of-the-Art Deep UV Resists

(Task number: 425.033)

Catalyzed Hydrogen Peroxide (CHP) Systems For High Dose Implat Stripping (HDIS)

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Industrial Mentors:

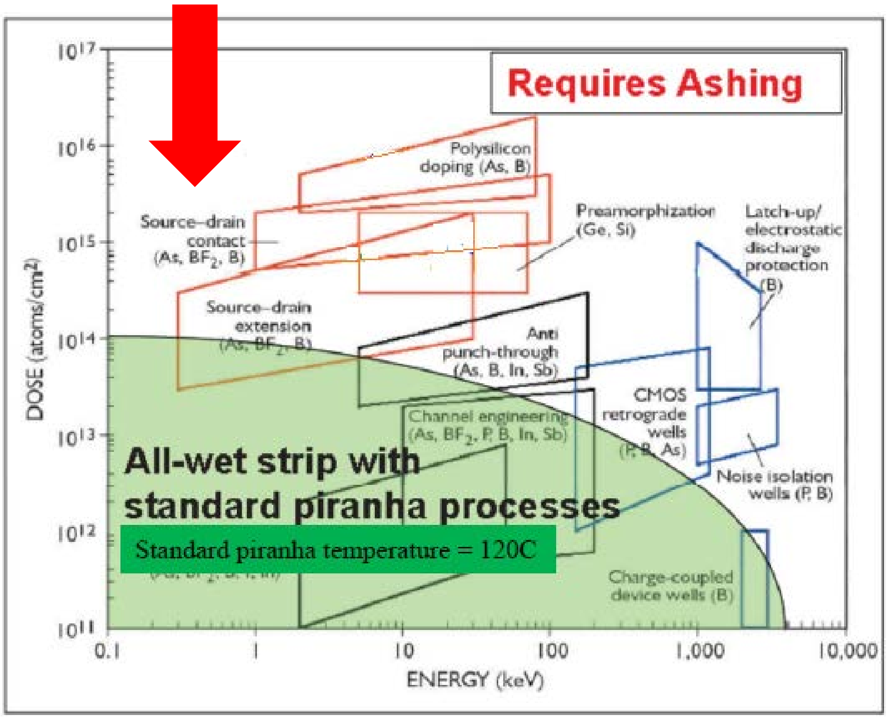
- **Dr. Ian Brown, TEL**
- **Dr. Jeff Butterbaugh, FSI-International**

Cost Share (other than core ERC funding):

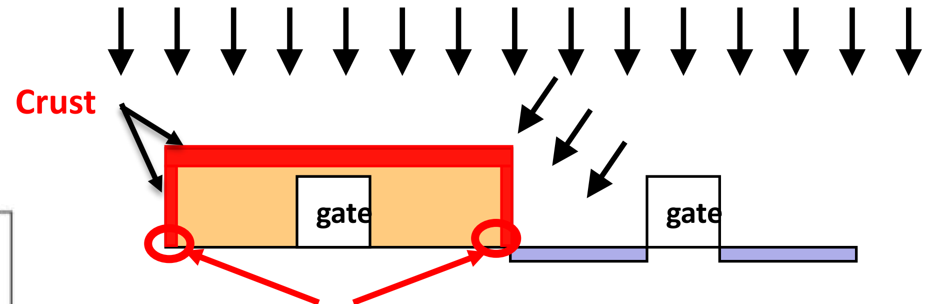
- **In-kind donation of ion-implanted resist wafers by *Sematech*(~ $ 5,000), and TEL (~$3,000); Testing at TEL (cost unknown)**

Challenge

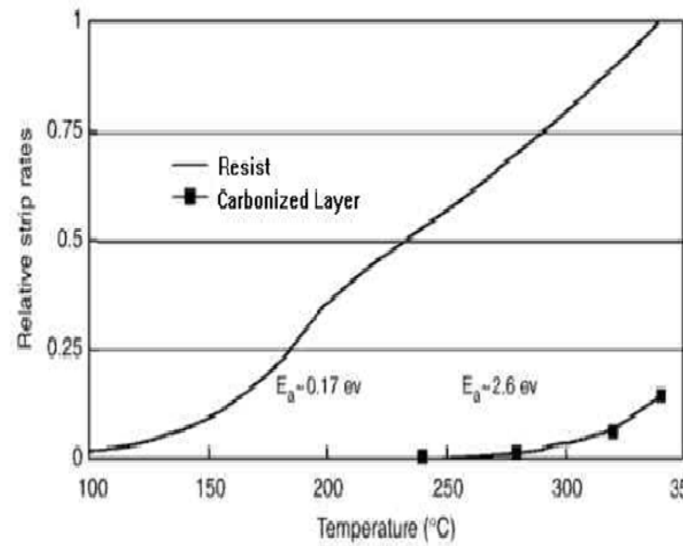
High Dose Implant



Reference: J.W. Butterbaugh, *SPCC presentation*, Austin, TX, May, 2006



Most challenging where crust is fused to wafer surface; also near EBR region



Reference: Robert Doering and Yoshio Nishi, *Handbook of Semiconductor Manufacturing Technology* (CRC Press, 2007).

- **High dose ions create a crust layer that makes resist stripping difficult**

Objectives

Overall Objective:

- **Development of an environmentally friendly process based on catalyzed hydrogen peroxide systems (CHP) for stripping high dose implanted resists**

Goals for the three year period (2009-2011)

- **Investigate the use of hydrogen peroxide activated by UV light or metal ions for disrupting crust formed on photoresist (PR) layers exposed to high dose of ions ($\geq 10^{15}$ /cm^2)**
- **Evaluate the stripping of pre-treated PR with low temperature (<120^{0}C) SPM containing low levels of peroxide**
- **Collaborate with TEL to test the two step process on patterned implanted resist samples using an industrial tool**
- **Compare the efficacy of the developed 2-step process with FSI's VIPR process**

ESH Metrics and Impact

- **SPM solution**
  - Requires high temperature (> 200^0C) for stripping high dose implanted resists

- **Comparison of toxicity of ingredients in CHP and SPM**

Compound	LD_{50}	Carcinogenic
Hydrogen Peroxide	2000 mg/kg (mouse)	NO
Sulfuric acid	90 ml/kg (rat)	Yes
UV light (216nm)	3 mJ/cm^2 (Bacteria)	Yes

- **ESH Impact**
  - By using low temperature (< 120^0 C) SPM as a chemical in the second step, ***energy and safety issues related to the use of very hot SPM can be significantly reduced***

Experimental Approach

Investigation of CHP System

Metal Catalyst

Fe^{2+}

UV Catalyst

12.2 mW/cm^2

Implanted Photoresist

Dose: 1E15 & 16 As/cm^2

***Source:* Sematech, FSI**

***Thickness:* ~ 1.5 µm**

Immersion Process

Spin/Puddle Process

Characterization

Screening:

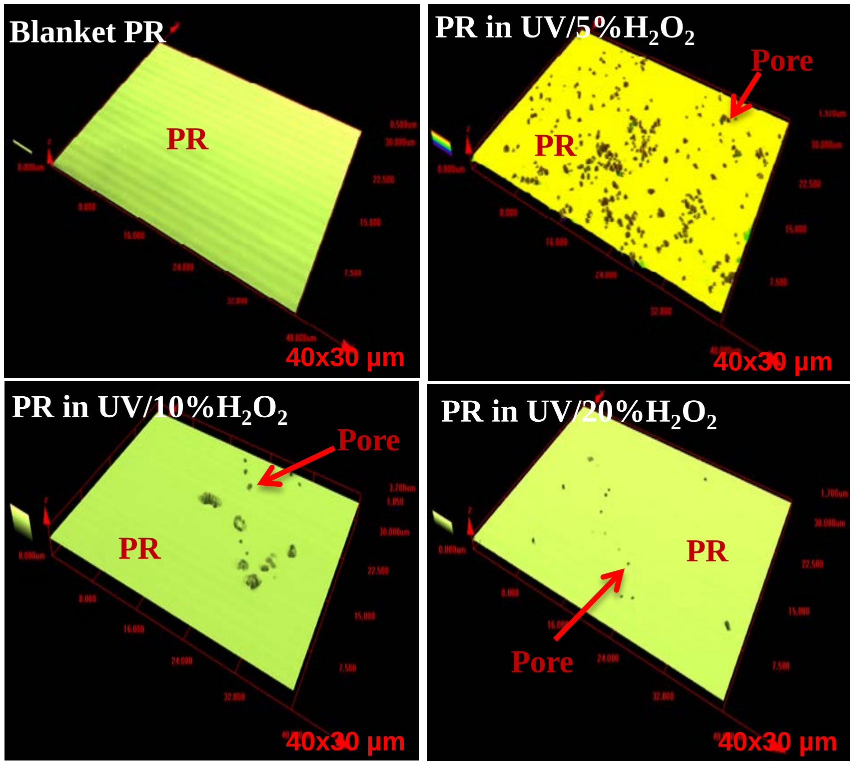
- **FESEM** ***(Hitachi S-4800)***
- **Confocal Microscope** ***(Leeds)***

Confirmation:

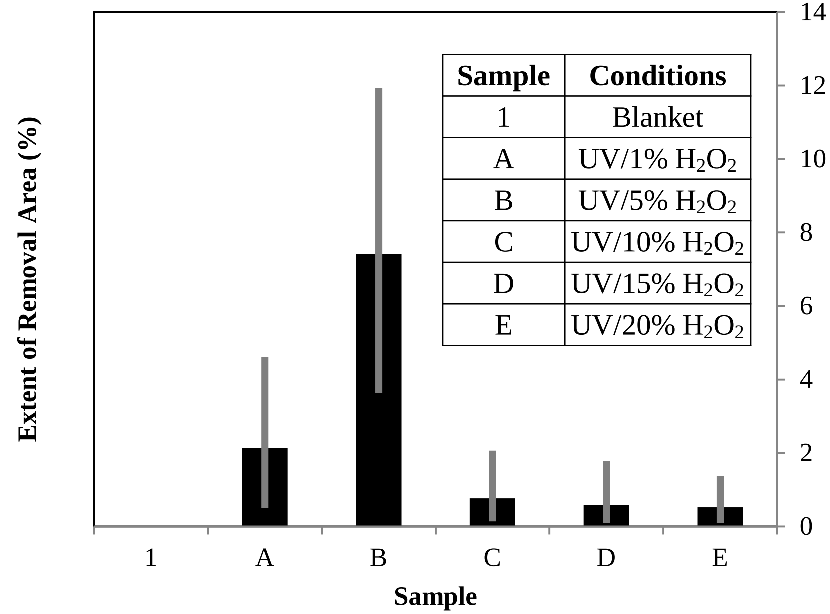
- **XPS** ***(Kratos Axis Ultra)***
- **EDS** ***(Hitachi S-4800)***

Effect of UV Activated H_2O_2 on Implanted PR (Dose: 1E 16 As/cm^2)

3D Confocal Micrographs



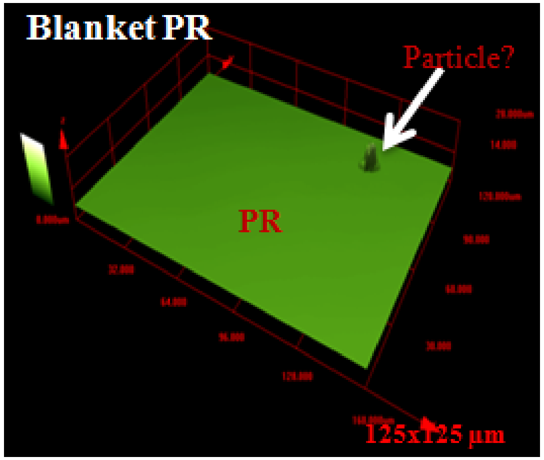
Effect of H_2O_2 Concentration on PR disruption under UV irradiation



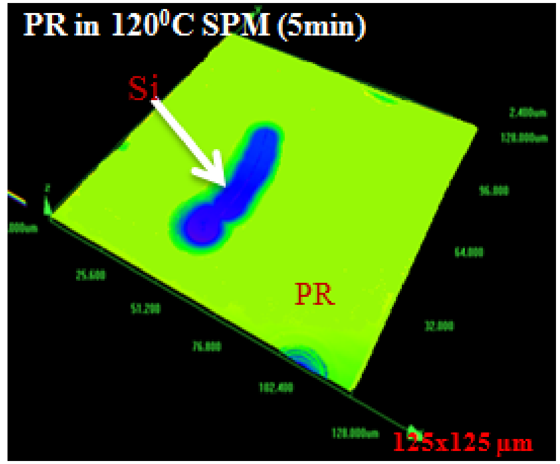
- **Implanted PR exposed to UV (12.2 mW/cm^2) irradiated H_2O_2 (15 ml/min) at 40^0C for 15 minutes**
- **Good attack observed with 5% H_2O_2 activated by UV light (confirmed using Tukey Kramer Statistical analysis)**
- ***Extent of disruption/attack depends on H_2O_2 concentration***

Effect of SPM & Two Step UV-H_2O_2/SPM Process

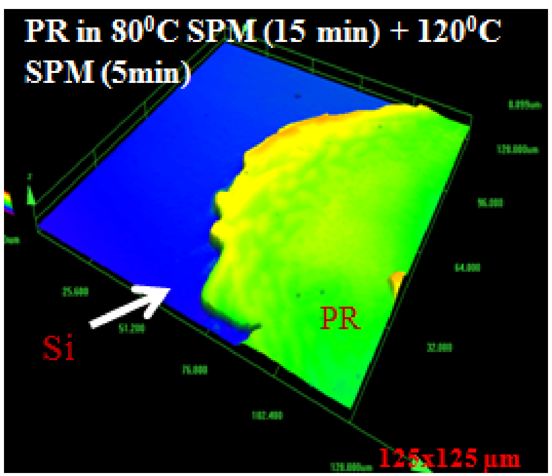
3D Confocal Micrographs



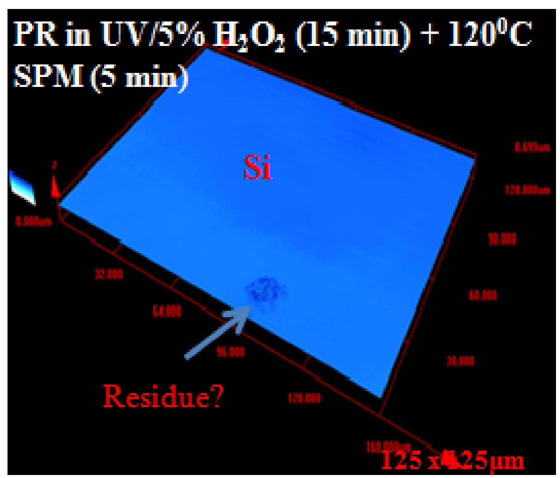
Untreated Sample



Inefficient removal



Reduced extent of removal



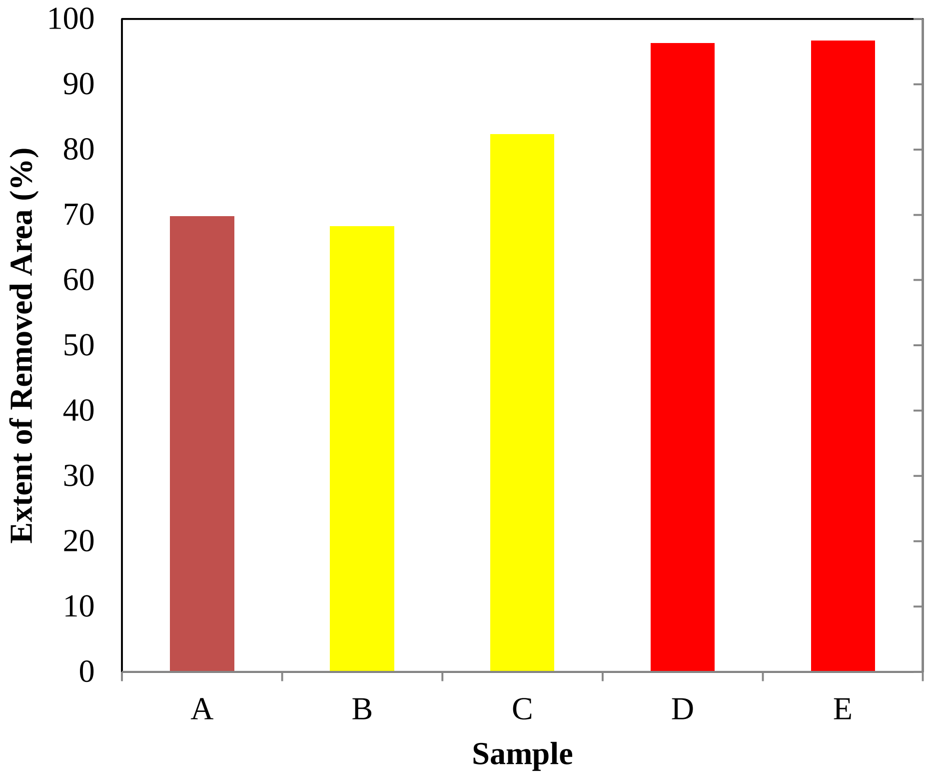
Complete removal

- **SPM treatment – localized PR removal (bare Si as blue color) 2:1 SPM: Preheated (80^{0}C) H_2SO_4 mixed with H_2O_2, solution dispensed at ~ 120^0 C**

- ***Two step process involving UV/ 5% H_2O_2 exposure followed by 2:1 SPM (120 ^{0}C) treatment results in very good removal of PR***

Refinement of SPM based Second Step

Variable: SPM ratio & H_2O_2 concentration



Step I: 15 minutes
Step II: 5 minutes

- **Step I (same for all samples)- 5% H_2O_2 @ 40^0C irradiated with $12.2mW/cm^2$ UV intensity;**
- **Step II – SPM treatment using H_2SO_4 preheated to 80^0C mixed with H_2O_2 at room temperature**

- **Good PR removal is possible in SPM containing as low as 0.2% H_2O_2**

Sample	Condition	Net H_2O_2 level	Final Temperature (~ ^0C)
A	H_2SO_4 (4 parts)+ H_2O (1 part)	0	110 - 120
B	H_2SO_4 (2 parts)+ 1% H_2O_2 (1 part)	0.33%	
C	H_2SO_4 (2 parts)+ 5% H_2O_2 (1 part)	1.6%	
D	H_2SO_4(4 parts) + 1% H_2O_2 (1 part)	0.2%	
E	H_2SO_4(4 parts) + 5% H_2O_2(1 part)	1.0%	

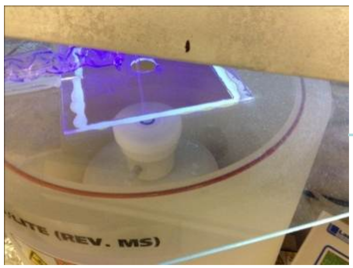
INDUSTRIAL COLLABORATIONS

TEL Results

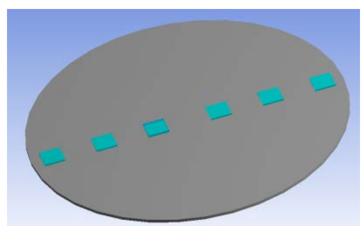
- **Patterned (L/S) DUV photoresist samples exposed to As ion beam (5 E15/cm2) were provided by Dr. Ian Brown of TEL**
- **These were first treated at the University of Arizona using the UVAP process (First step)**
- **Treated samples were shipped to TEL application laboratory for second step (SPM) treatment. TEL's objective was to *determine the lowest possible temperature of the SPM step* that will still yield good stripping.**

Resist Strip Performance Comparison between Benchtop SPM and a 300mm SPM Spin Tool (SPM temperature is kept constant at 120C)

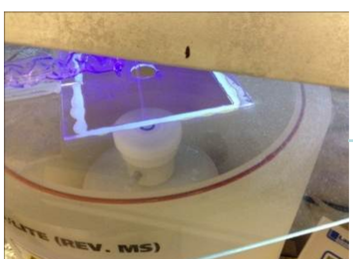
Benchtop 120C SPM

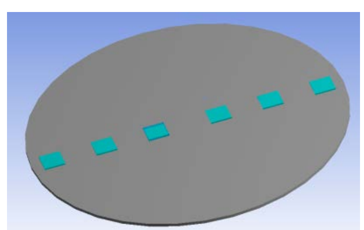


Bench top UVP + 120C SPM



300mm Spin Tool 120C SPM

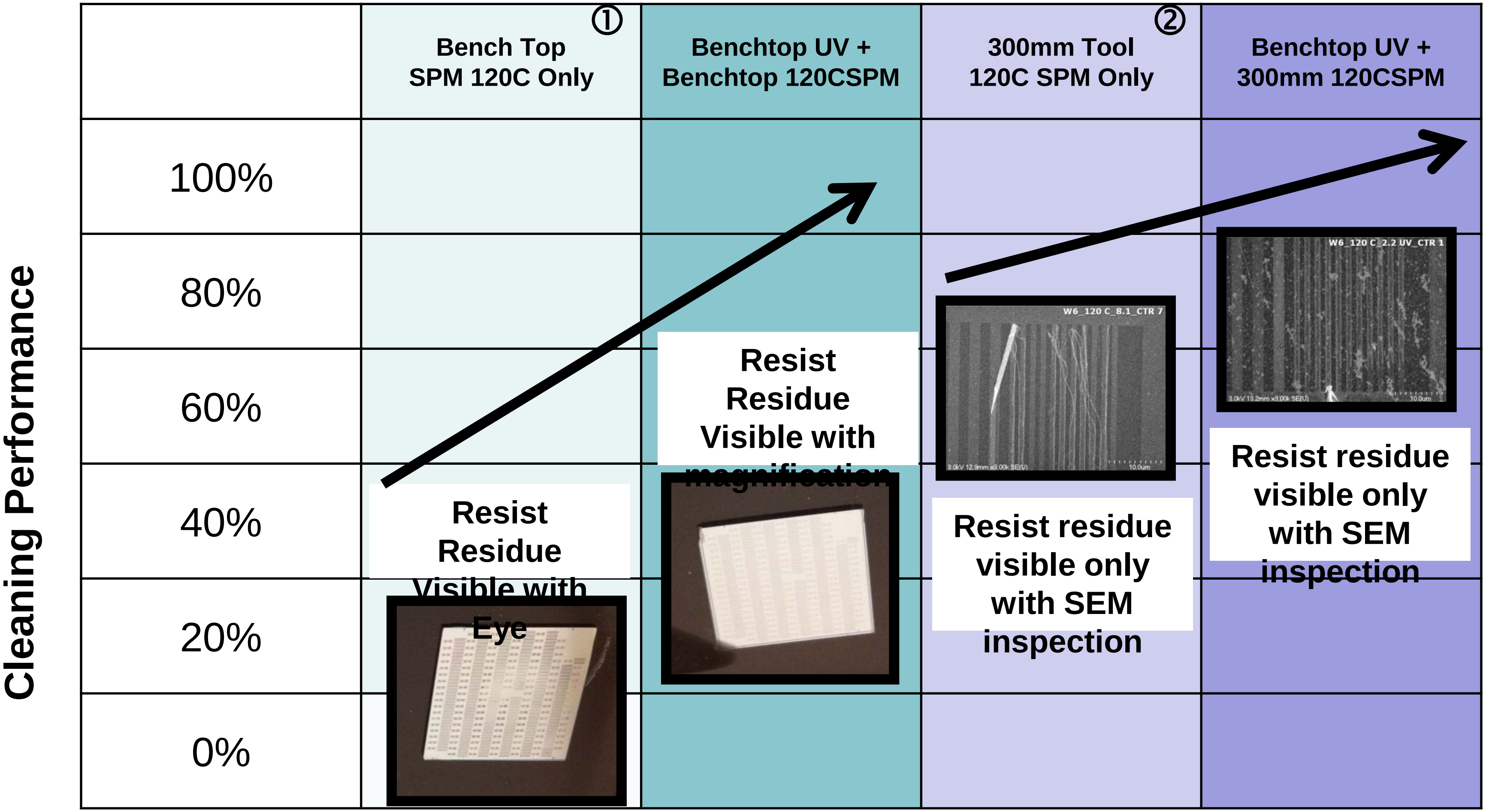




Benchtop UVP +
300mm Spin Tool 120C SPM

300mm Spin Tool removed resist more effectively than Benchtop Hardware

UV process showed less improvement with the 300mm SPM process compared to the Benchtop SPM process

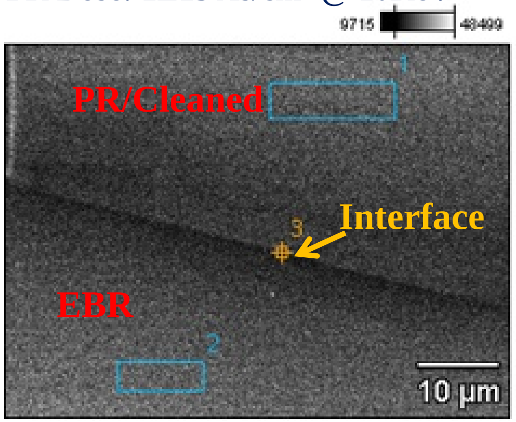


① Benchtop resist removal performance was significantly improved with a 5 min SPM process (50%) but for this benchmarking test process times were kept constant at 1 min for both benchtop and 300mm tool.

② In a separate test the 300mm spin tool using higher temperature SPM was able to completely clean the 5E15 As doped resist sample.

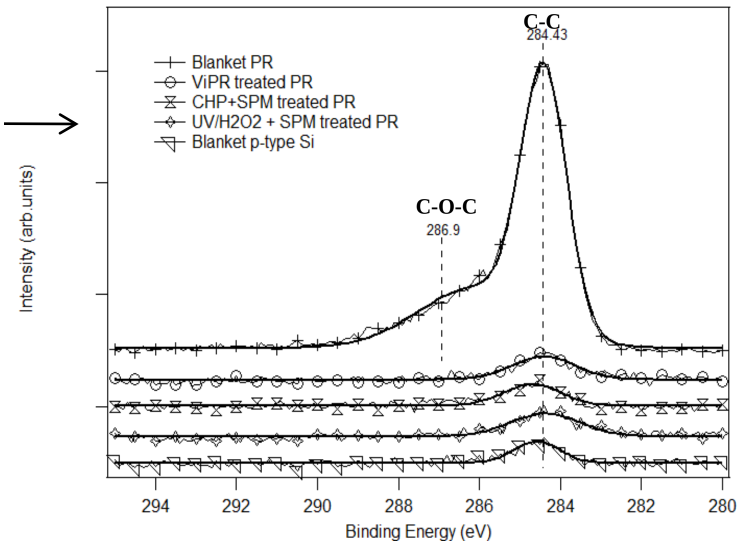
Comparison of FSI ViPR Process® with CHP Based Two Step Treatment

Sample Provided by FSI
PR Dose: 1E15 As/cm^2 @ 10KeV

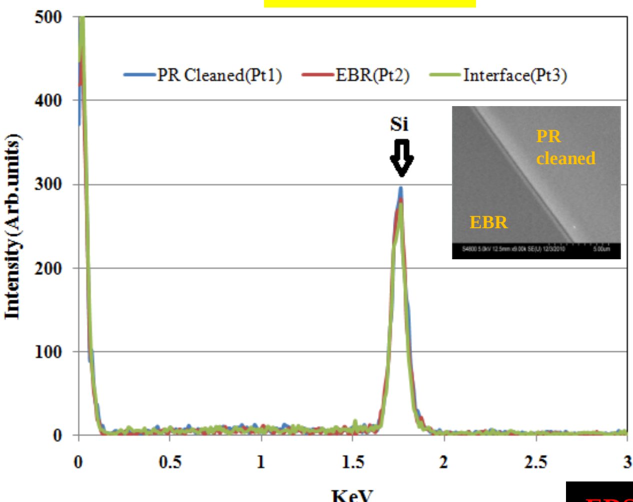


ViPR® Cleaned EBR (Edge Bead Removal) Region
Interface – Difficult to remove

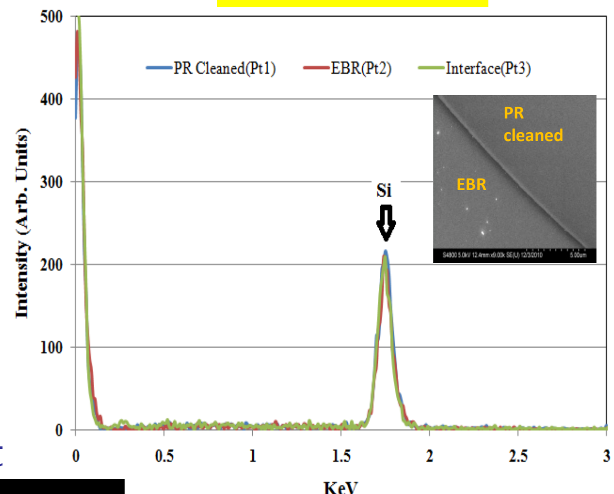
XPS Spectrum



ViPR Clean



CHP+SPM Clean



EDS Spectrum

XPS:

- **XPS analysis shows dominant C-C peak at interface region for blanket Implanted PR**
- **XPS Spectrum of treated samples are similar to that of blanket Si – complete PR removal**

EDS:

- **Sample cleaned using ViPR process strips PR *(no C & O signal)***
- **CHP & UV/H_2O_2 treatment (15 mins) followed by 2:1 SPM (~120^{0}C, 5 mins) *shows similar result as ViPR process***

Summary

- **H_2O_2 solution activated by exposure to UV at 40 ^{0}C creates surface defects on high dose implanted PR**

- ***Good removal of high dose implanted PR is possible by first exposing the resist in UV irradiated 5% H_2O_2 solution for 15 minutes and then in 2:1 SPM at ~120 ^{0}C for 5 minutes under spin conditions***

- **PR removal is possible in SPM containing as low as 0.2% H_2O_2**

- **Developed two step process has shown some benefits when practiced on a TEL 300 mm single wafer tool**

Publications, Presentations and Patent

- **Patent on "Enhanced Stripping of Implanted Resists", was filed by SRC in December 2010 (File No: US 12/981,073)**
- **"Effect of Pretreatment of High Dose Implanted Resists by Activated Hydrogen Peroxide Chemical System for their Effective Removal by Conventional Sulfuric-Peroxide Mixtures", accepted for publication in *IEEE Transactions on Semiconductor Manufacturing (2012)*.**
- **R. Govindarajan, M. Keswani and S. Raghavan, "Effect of Pretreatment of High Dose Implanted Resists by Activated Hydrogen Peroxide Chemical System for their Effective Removal by Conventional Sulfuric-Peroxide Mixtures", TECHCON Conference, Austin, TX, Sep 12-13 (2011)**
- **R.Govindarajan, M.Keswani and S.Raghavan, "High Dose Implant Resist Stripping (HDIS) Using Catalyzed Hydrogen Peroxide (CHP) Systems", 219th ECS Meeting in Montreal, Canada, May 1 - 6 (2011).**

Acknowledgements

- Ian Brown of TEL, Jeff Butterbaugh of FSI
- **Bob Morris (Oclaro) and Dr. Manish Keswani (Univ. of AZ)**