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

(Task number: 425.033)

Experimental Investigation of Catalyzed Hydrogen Peroxide (CHP) System For HDIS

PI:

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Cost Share (other than core ERC funding):

- **In-kind donation of ion-implanted resist wafers by *Sematech*(~ $ 5,000) and FSI International (~ $ 2,000)**

Objectives

Overall Objective:

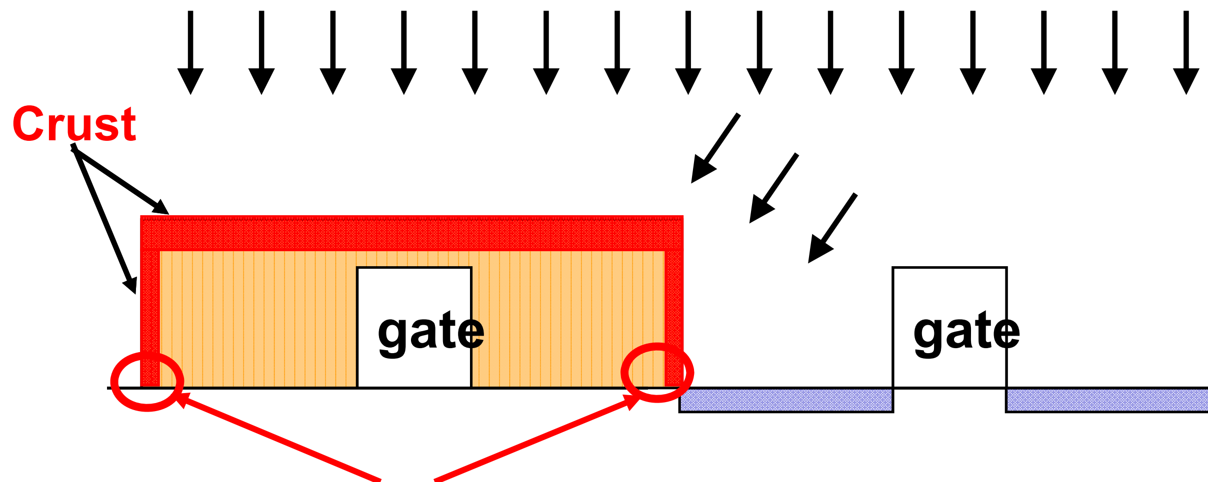
- **Development of an environmentally friendly process for stripping high dose implanted resists using catalyzed hydrogen peroxide system (CHP)**

Current Year Goals:

- **Eliminate/reduce the use of iron in Catalyzed hydrogen peroxide (CHP) system**

- **Investigate the use of UV activated Hydrogen Peroxide system for disrupting crust formed on resist layers exposed to high dose of ions ($\geq 10^{15}$ /cm^2)**

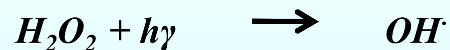
Stripping Implanted Photoresist



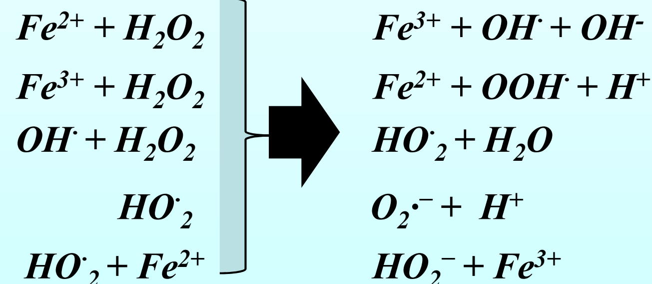
➢ Currently, high temperature (>200 ^{0}C) SPM is used to attack crust & resist

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

H$_2$O$_2$ Activation by UV light



Catalyzed H$_2$O$_2$ Propagation



➢ Radicals- strong oxidants

➢ CHP system disrupts crust and provides access to SPM

Perhydroxyl radical ($HO^{\cdot}_2$ – weak oxidant);
Superoxide radical anion($O_2^{\cdot -}$ - nucleophile)
Hydroperoxide anion (HO_2^{-} - strong nucleophile)

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
Ferrous sulfate	1520mg/kg (mouse)	NO
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 secondary chemical, ***energy and safety issues related to the use of very hot SPM can be significantly reduced***

Current Year Activities

- **Carried out studies on spin tool for disrupting crusted resist using Catalyzed Hydrogen Peroxide (CHP) system**

- **Explored the use of UV activated Hydrogen Peroxide system for disrupting crust that typically forms on high dose implanted resists**

- **With permission from FSI, characterized wafers subjected to their proprietary steam activated SPM process (ViPR®); compared effectiveness of CHP/SPM process with ViPR® process**

Experimental Approach

➢Materials

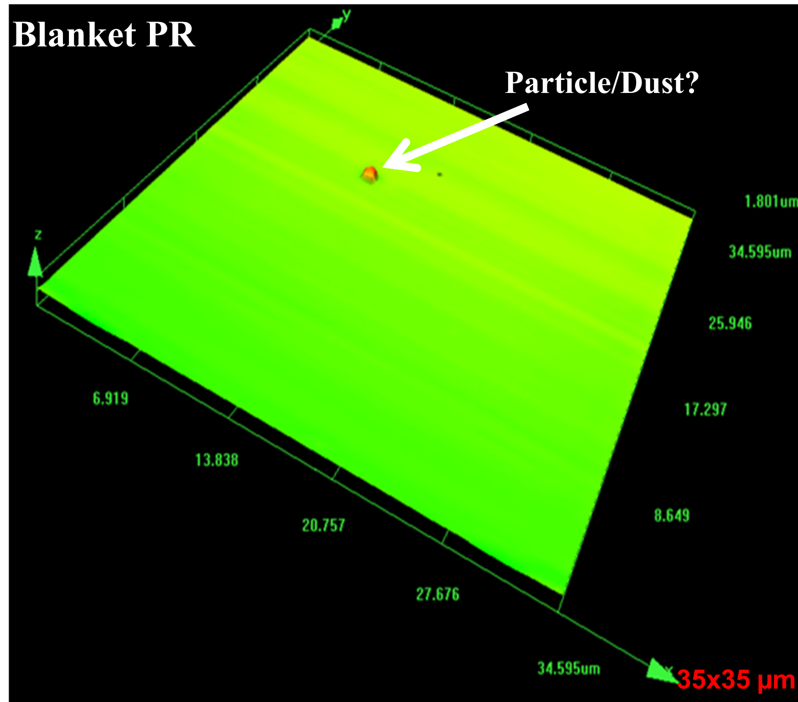
- **Implanted resist films (1E16 As /cm^2 ; ~1.5 µm) donated by Sematech, (1E15 As /cm^2 ~1.0 µm) FSI International**
- **UV light source (Wavelength: 254nm; Intensity : 12.2 mW/cm^2 at 3”)**
- **Ferrous Sulfate ($FeSO_4 . 6H_2O$) , 99.998% pure**
- **Hydrogen Peroxide (30%)**

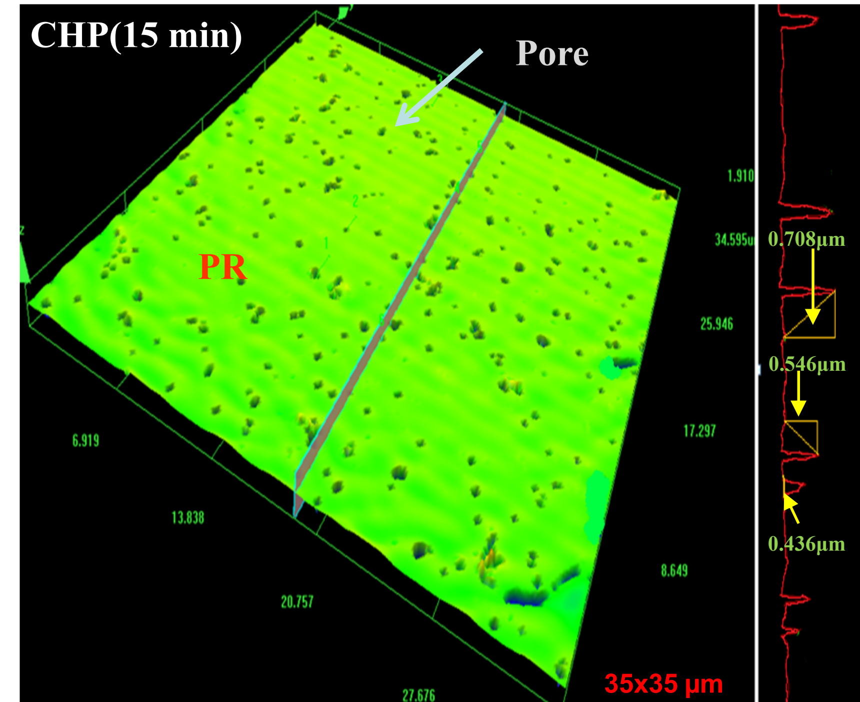
➢Methods

- **Experiments conducted on Laurell Spinner using puddle method (dispensing solution, allowing it to stay, followed by spinning)**
- **Morphological changes after CHP treatment were characterized using Leica DM4000B microscope operated using QCapture Pro 5.0 software, Leeds Confocal microscope, FESEM and XPS**

Effect of CHP Treatment on Implanted PR

3D Confocal Micrographs





AS IMPLANTED

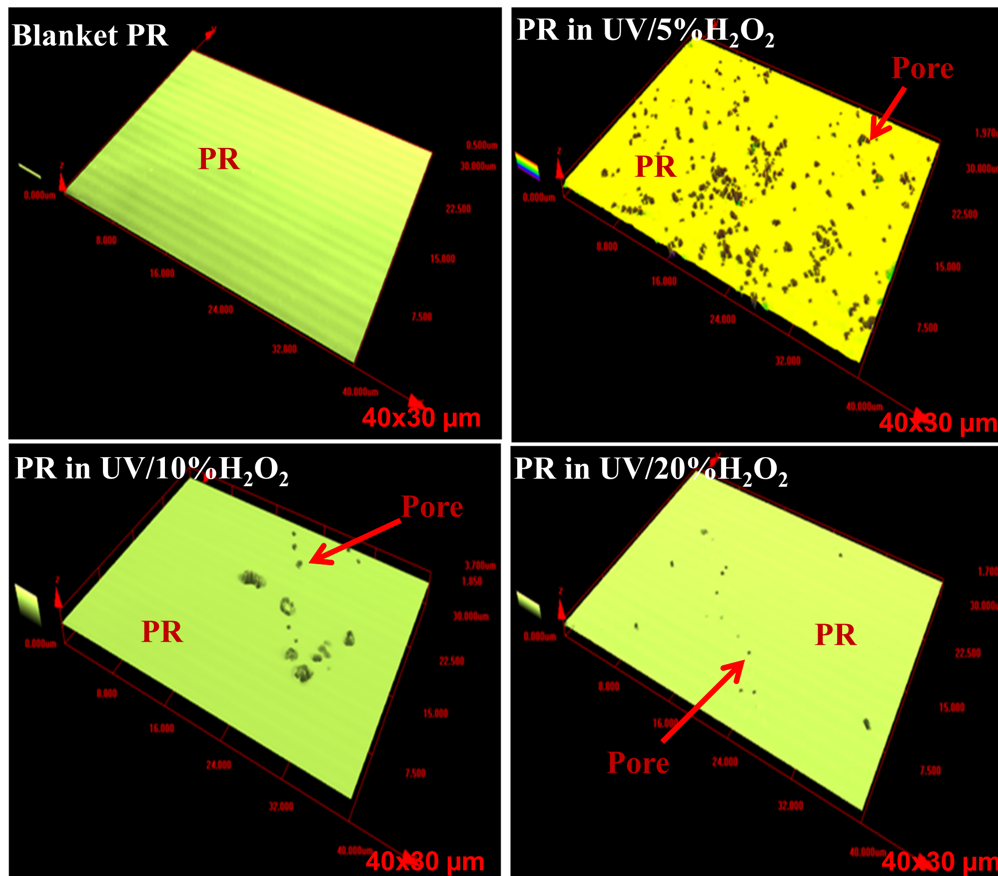
TREATED WITH CHP

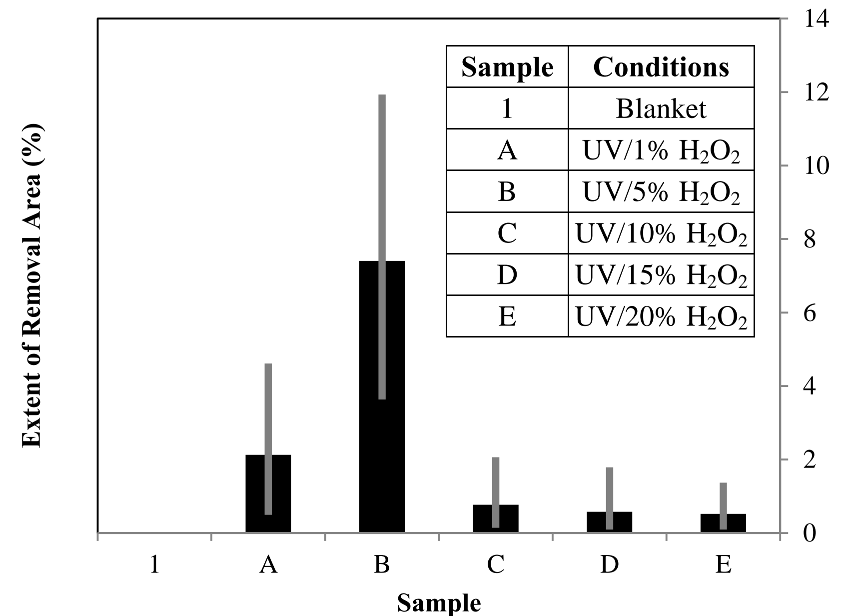
- Blanket PR (dose: 1E16 As/cm^2) is smooth without any pores
- CHP (5mM Fe^{2+}, 20% H_2O_2) treatment @ 25^{0}C for 15 minutes shows localized attack

PR surface has pores of depth < 700 nm and size < 1.5 µm

Effect of UV Activated H_2O_2 on Implanted PR

3D Confocal Micrographs



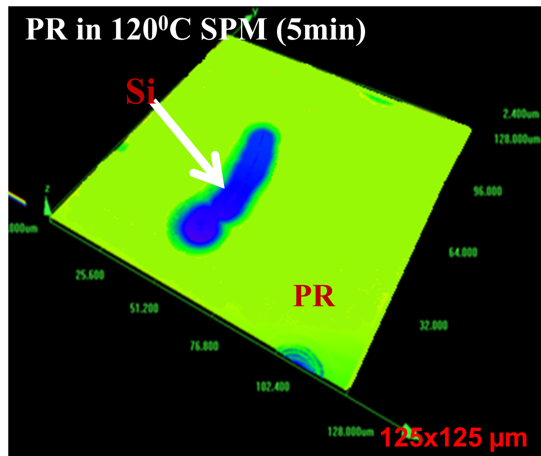


Sample	Conditions
1	Blanket
A	UV/1% H_2O_2
B	UV/5% H_2O_2
C	UV/10% H_2O_2
D	UV/15% H_2O_2
E	UV/20% H_2O_2

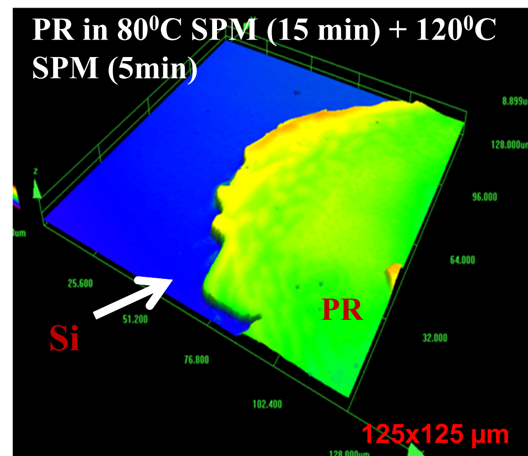
- **PR (dose: 1E 16 As/cm^2) exposed to UV irradiated H_2O_2 at 40^{0}C for 15 minutes**
- **Good attack observed with 5% H_2O_2 activated by UV light**
- ***Extent of disruption/attack depends on H_2O_2 concentration***

Effect of SPM & Two Step CHP(or UV-Peroxide)/SPM Process

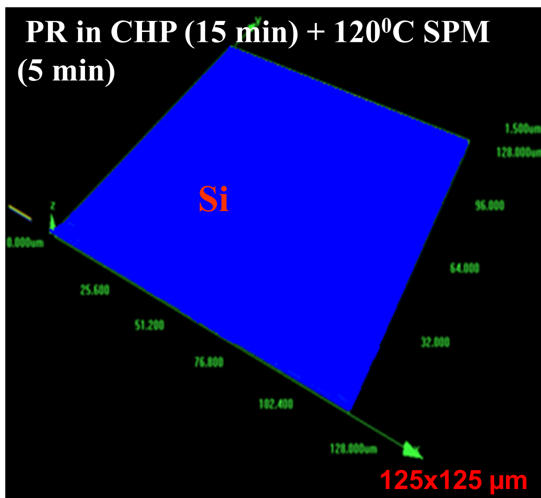
3D Confocal Micrographs

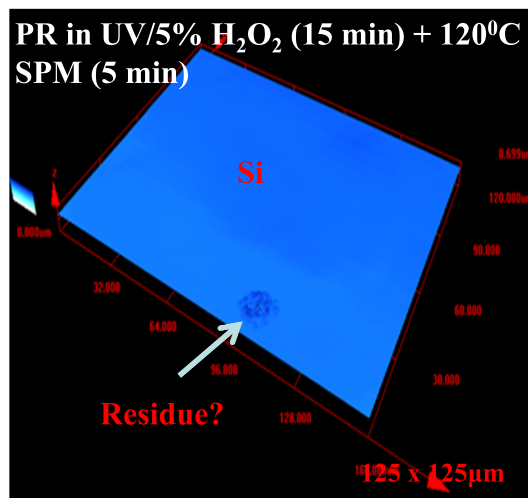


Inefficient removal



Reduced extent of removal



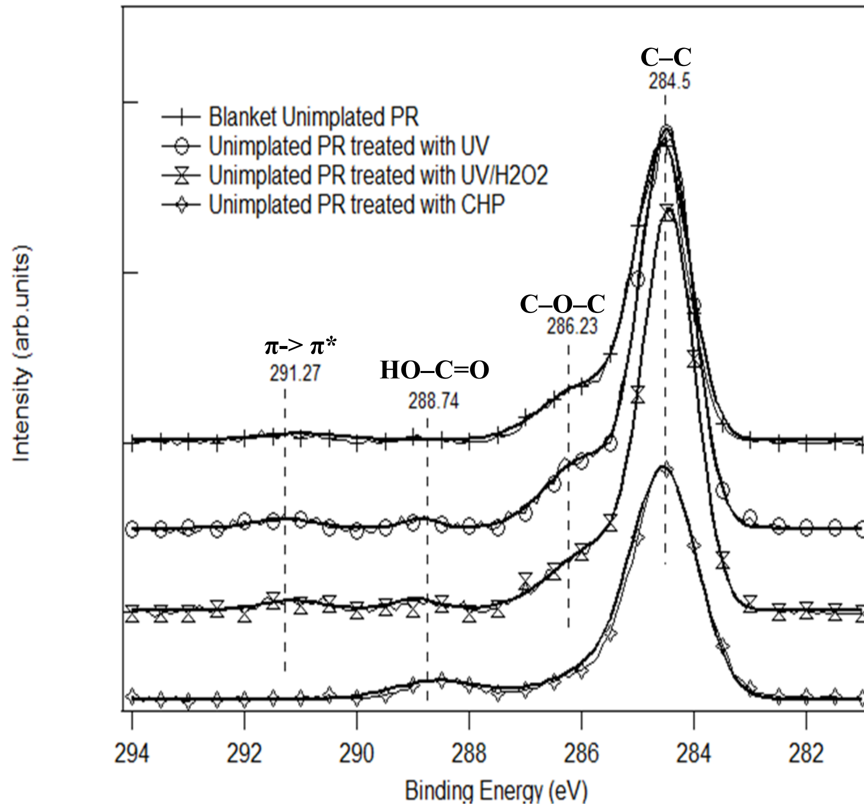


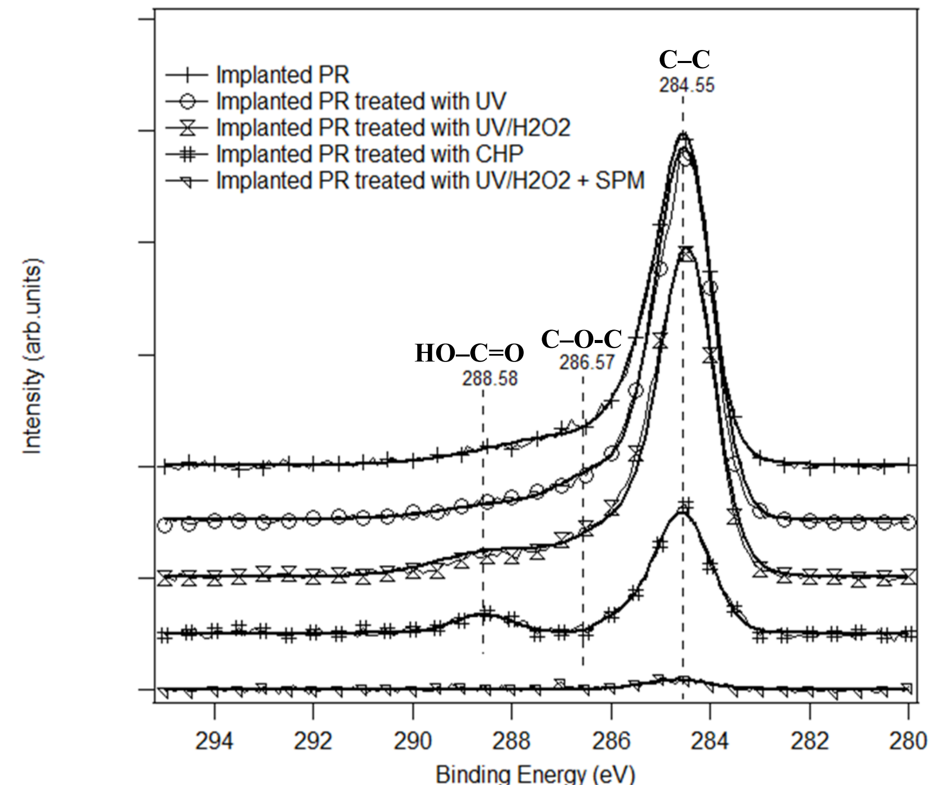
Complete removal

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

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

XPS analysis of PR film after different treatments

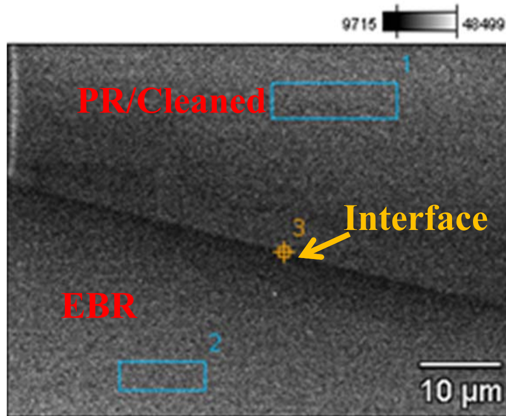




- Unimplanted and Implanted PR show dominant C-C peak with some C-O-C
- UV/H_2O_2 & CHP treated samples contain carboxyl groups
- Stripping of implanted PR by UV/H_2O_2 followed by SPM leaves a surface with trace amount of carbon

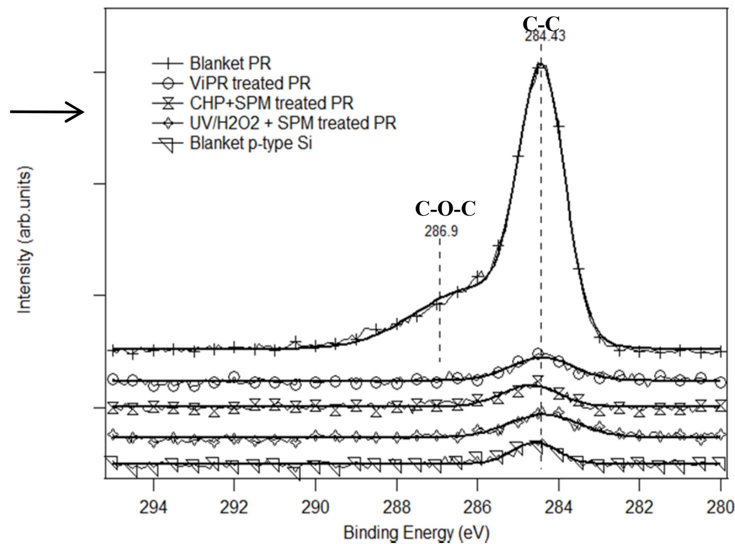
Comparision of FSI ViPR® Process with CHP Based Two Step Treatment

Sample Provided by FSI
PR Dose: 1E15 As/cm² @ 10KeV

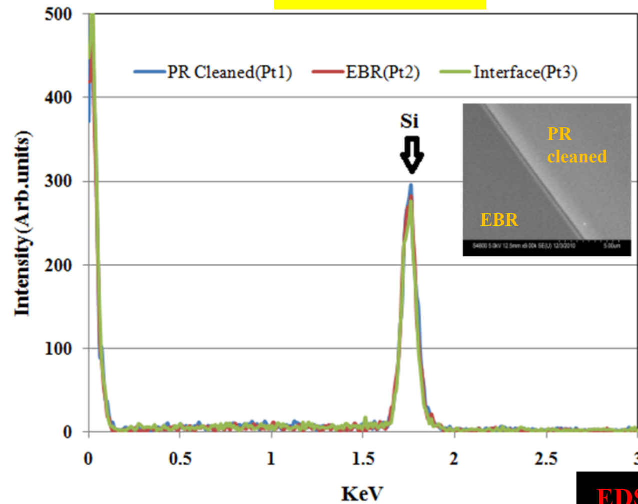


ViPR® Cleaned EBR (Edge Bead Removal) Region
Interface – Difficult to remove

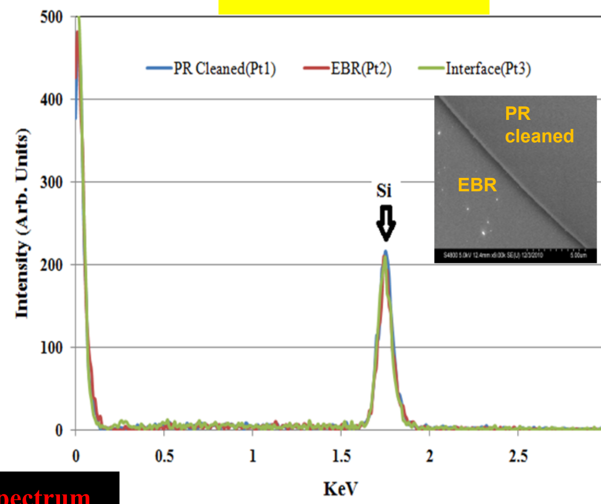
XPS Spectrum



ViPR Clean



CHP+SPM Clean



EDS Spectrum

XPS:

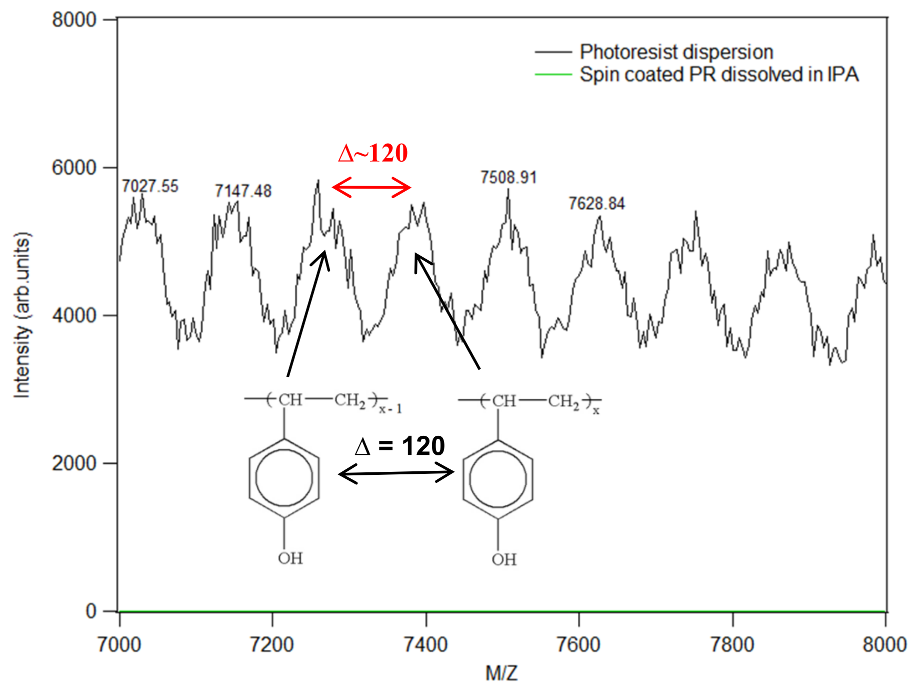
- XPS analysis shows dominant C-C peak at interface region for blanket Implanted PR
- XPS Spectrum of treated samples are similar to that of blanket Si – complete PR clean

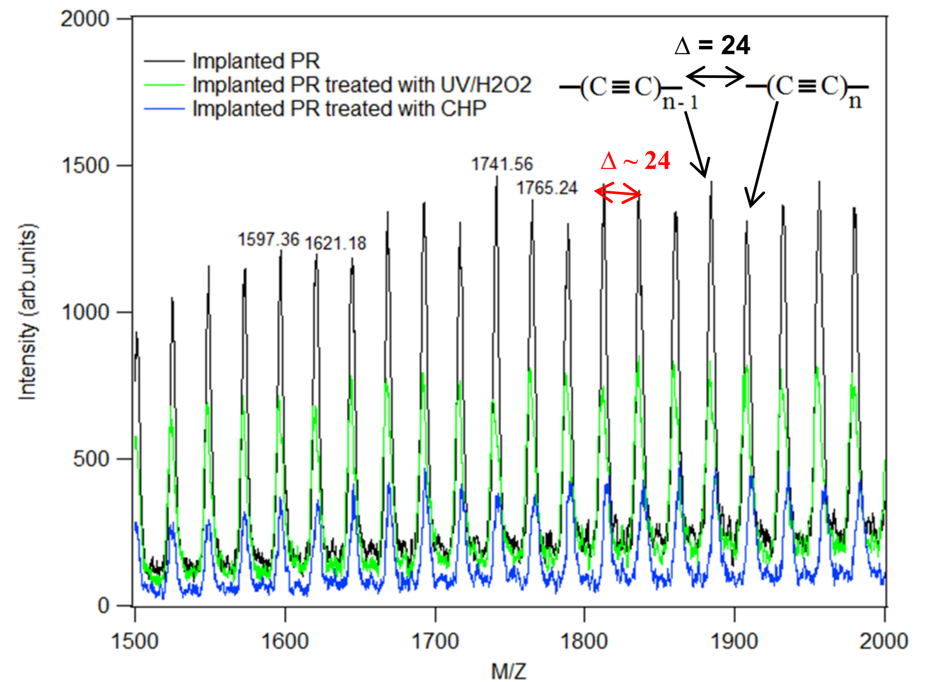
EDS:

- 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*

Preliminary Investigation of Crusted PR Using LDI-MS

(Laser Desorption/Ionization – Mass Spectroscopy)





➢**Molecular weight of fragments from liquid resist differs by 120 amu, corresponding to hydroxystyrene unit**

➢**Spin coated PR film dissolved in IPA shows no signal; fragments released too large to be effectively ionized -- Needs further study**

➢**Molecular weight of fragments from implanted (1E16 As/cm^2) resist differs by 24 amu, corresponding to carbyne (C≡C) unit; crust is carbonized**

Summary

- **CHP system containing 5 mM Fe^{2+} and 20% H_2O_2 at 25 ^0C and 5% H_2O_2 exposed to UV at 40 ^0C create surface defects on high dose implanted PR; modifies the chemical nature of crust**

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

- ***Effectiveness of two step CHP/SPM process appears comparable to that of FSI's ViPR process***

Deliverables Status

Promised Deliverables	Y/N/IP
Use of non-metal based catalyst to activate Hydrogen Peroxide	Yes; Using UV source
Work with Tool maker to test/compare the chemical system	Yes; For 1E15 As/cm^2 implanted samples with FSI's ViPR process
Evaluation of two step (CHP and UV irradiated H_2O_2 followed by conventional SPM) process to strip films	Yes

Future Plans

Next Year Plans

- **Optimization of UV activated hydrogen peroxide system to decrease the exposure time prior to conventional SPM treatment**

- **Explore the use of *non-metal catalysts* such as borates**

Long Term Plans

- **Investigate the use of sulfuric acid alone as the second step**

Industrial Interactions and Technology Transfer

- **Patent on "Enhanced Stripping of Implanted Resists", was filed by SRC in December 2010 (File No: US 12/981,073)**
- **R. Govindarajan, M. Keswani and S. Raghavan, "Development of an all wet benign process based on catalyzed hydrogen peroxide (CHP) chemical system for stripping of implanted state-of-the art Deep UV resists ", TECHCON Conference, Austin, TX, Sep 13-14 (2010)**
- **R.Govindarajan, M.Keswani and S.Raghavan, "High Dose Implant Resist Stripping (HDIS) Using Catalyzed Hydrogen Peroxide (CHP) Systems", accepted for presentation at the 219th ECS Meeting in Montreal, Canada, May 1 - 6 (2011)**
- **Interactions with Dr. Kanwal Singh of Intel on patterned wafers**
- **Technical discussions with Joel Barnett of Sematech & Jeff Butterbaugh of FSI International**

Acknowledgement

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