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 (wafers) from Sematech(~ $ 5,000)**

Objectives

- **Investigate the use of Catalyzed Hydrogen Peroxide (CHP) chemical system for disrupting the carbonized crust on deep UV resist layers exposed to high dose of ions ($\geqslant 10^{15}$ /cm^2)**

- **Identify the effectiveness of CHP system using amorphous carbon as model compound**

ESH Metrics and Impact

- **SPM solution**
  - Requires high temperature (~180^0C) for stripping high dose implanted resists

- **Low toxicity of CHP system**

Compound	LD_{50} (mouse)	Carcinogenic
Peroxide	2000 mg/kg	NO
Sulfuric acid	90 ml/kg (rat)	Yes
Ferrous sulfate	1520mg/kg	NO

- **ESH Impact**
  - Safety issues related to the use of very hot SPM can be significantly reduced

Current Year Activities

- **Explored the use of Catalyzed Hydrogen Peroxide (CHP) system for disrupting carbonized crust that typically forms on high dose implanted resists using amorphous carbon films as model compound**

- **Tested CHP system on ion-implanted resists**

- **Removal of the resist after disruption of crust was investigated using conventional SPM solutions at temperatures less than 80^0C.**

Experimental Approach

➢Methods

•Morphological changes after CHP treatment were characterized using Leica DM4000B microscope operated using QCapture Pro 5.0 software, Leeds Confocal microscope, AFM and FESEM

➢Materials

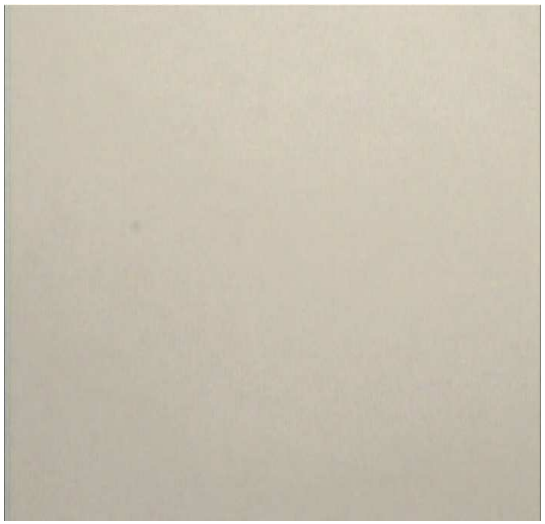
• Amorphous carbon films (~900 Å) donated by Applied Materials , Implanted resist films (1E16 As /cm^2 ; ~1.5 µm) donated by Sematech

•Ferrous Sulfate, 99.998% pure

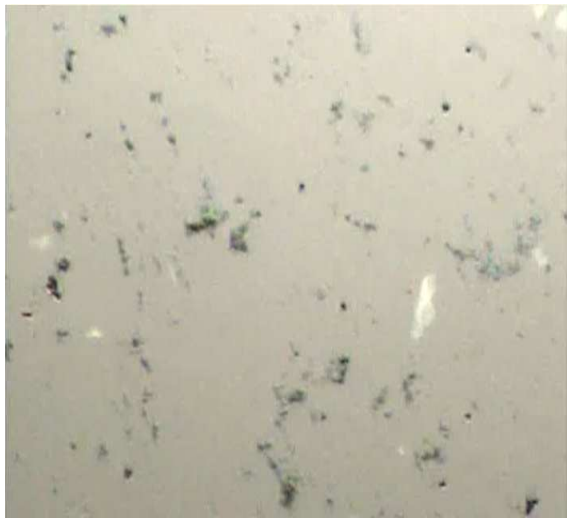
•Hydrogen Peroxide (Semiconductor grade)

Attack of Amorphous Carbon (a-C) Films

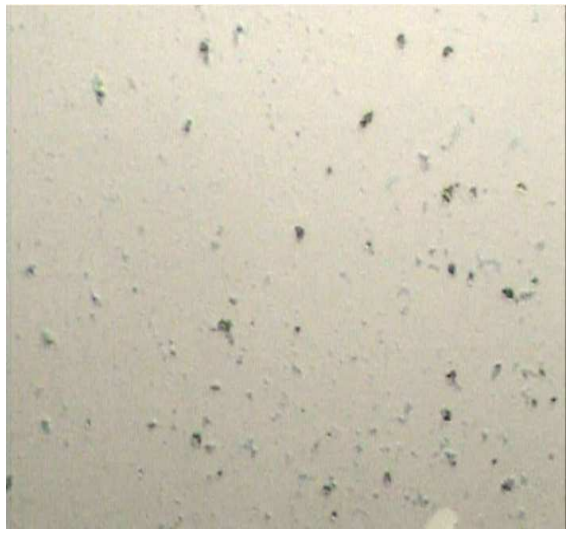
Optical Microscope Magnification : 1000x



Blanket a-C



a-C in 10% H_2O_2 CHP system



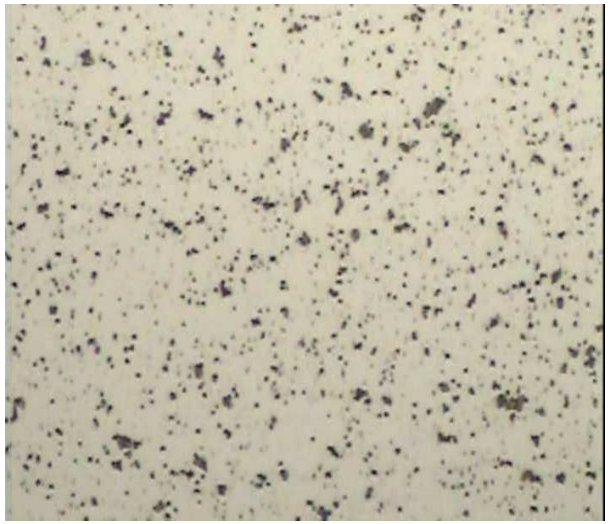
a-C in 20% H_2O_2 CHP system

- **CHP system: Hydrogen peroxide plus 1mM Fe^{2+}; pH: 2.8; room temperature**
- **Optical micrographs show disruption for one hour exposure**
- **Even after 15 minutes exposure, disruption was evident**

Effect of Fe^{2+} level in CHP on a-C disruption

Optical Microscope Magnification : 1000x

a-C in 1mM Fe^{2+} CHP system



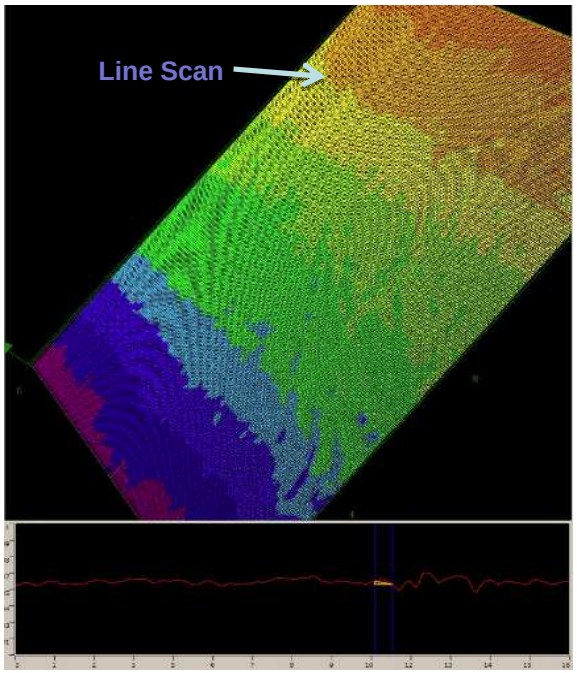
a-C in 5mM Fe^{2+} CHP system

a-C in 10mM Fe^{2+} CHP system

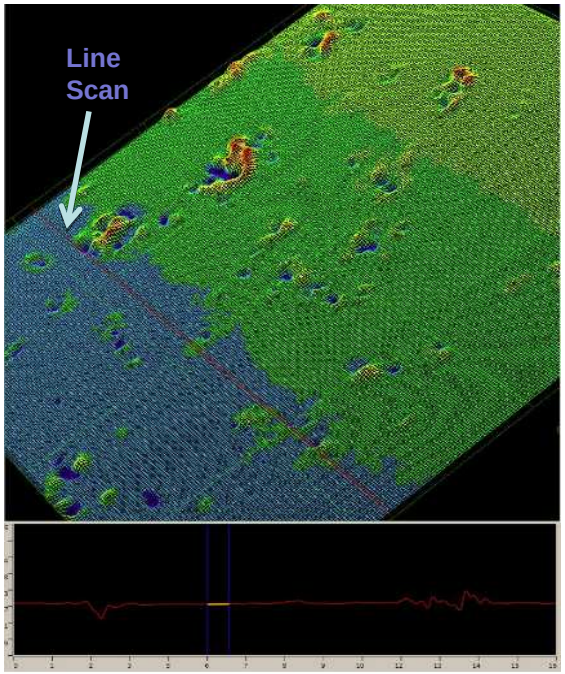
- **Experiments conducted for 30 minutes**
- **H_2O_2 concentration fixed at 20%**
- **Higher Disruption observed at 5mM Fe^{2+} level**
- **Poor attack in 10mM Fe^{2+} level CHP system may be due to faster decomposition of H_2O_2**

Confocal Microscopic Study of Changes in a-C film and High Dose Implanted Photoresist Film When Exposed to CHP

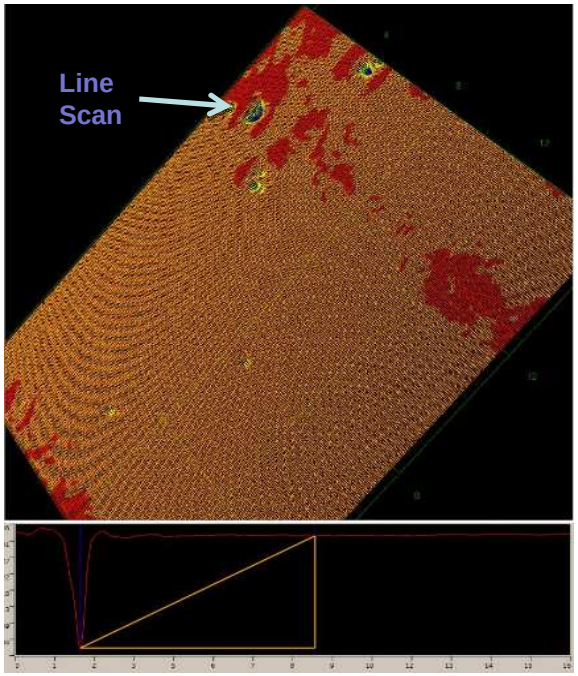
Confocal Microscope Magnification : 17Kx



Blanket a-C



a-C in 5mM Fe^{2+}, 20%H_2O_2

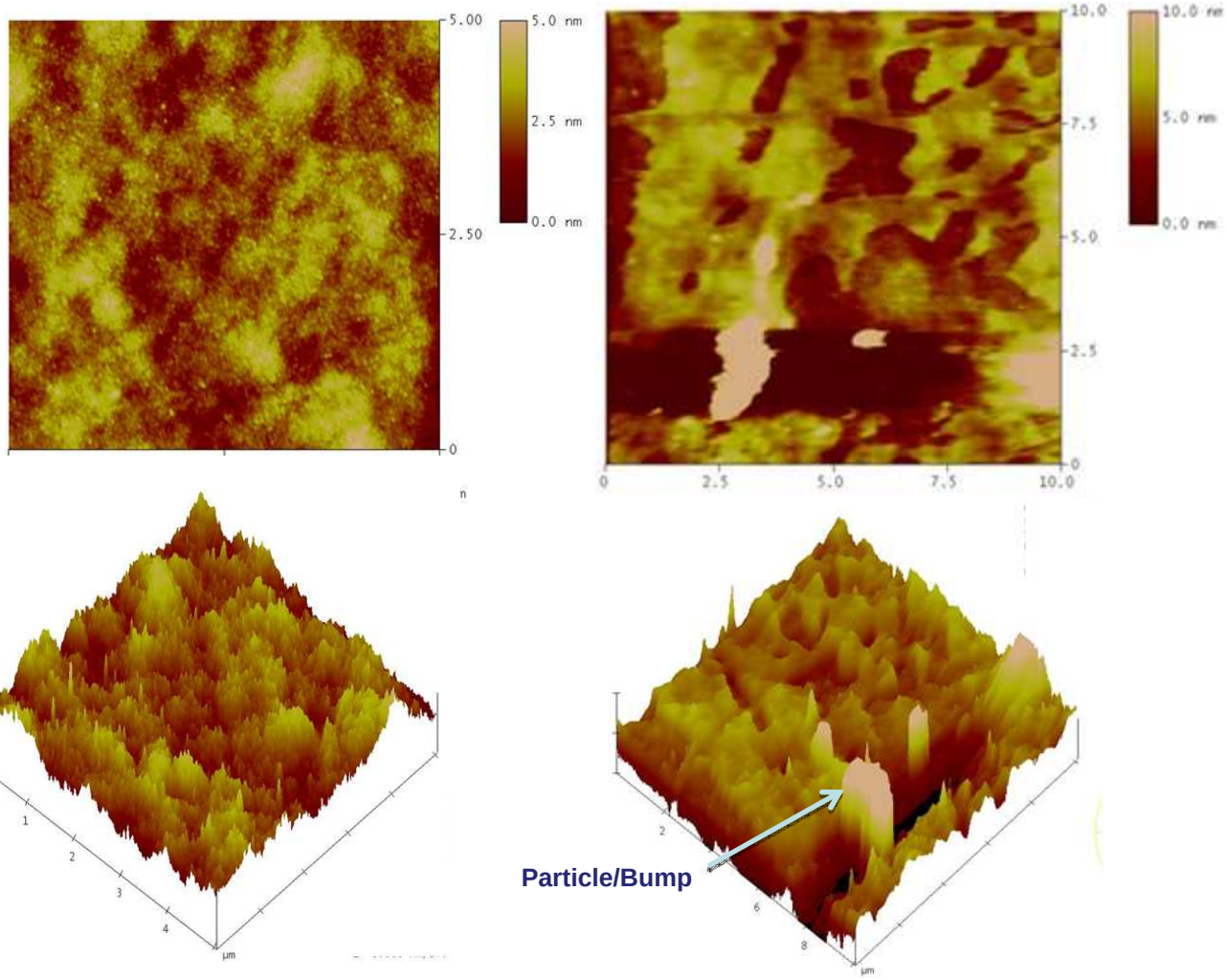


PR in 5mM Fe^{2+}, 20%H_2O_2

- **Effect of CHP on a-C and PR studied for 15 minutes**
- **Blanket a-C is smooth without pores**
- **CHP treated a-C shows disruption with depth up to 90 nm (~ film thickness)**
- **In high dose implanted PR (1E16 As/cm^2) pores of depth ~ 300 nm are seen**

AFM Analysis of Model a-C film

AFM Contact mode



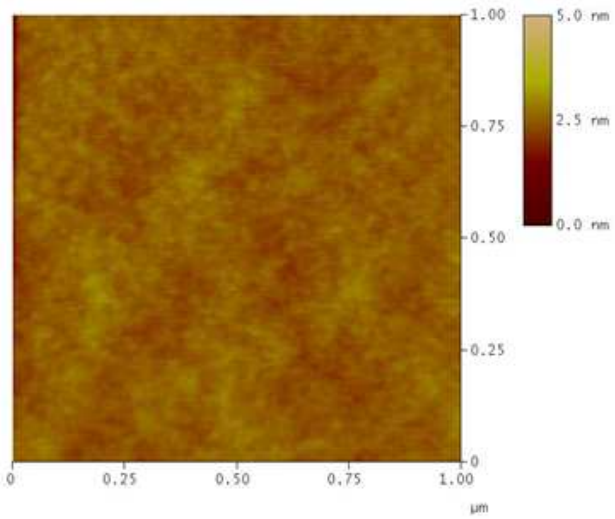
Blanket a-C

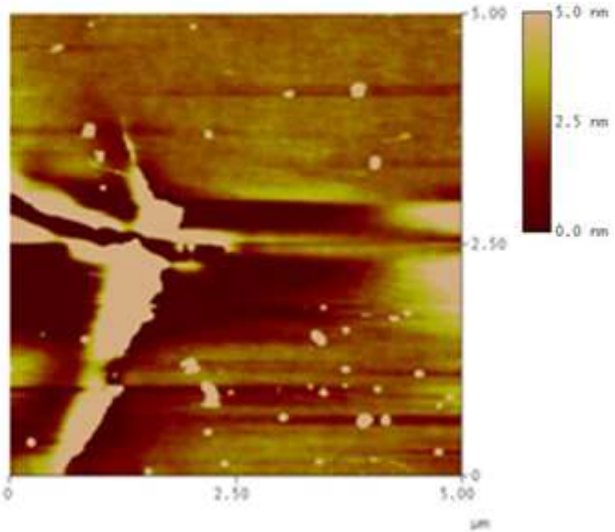
a-C in 5mM Fe^{2+}, 20%H_2O_2

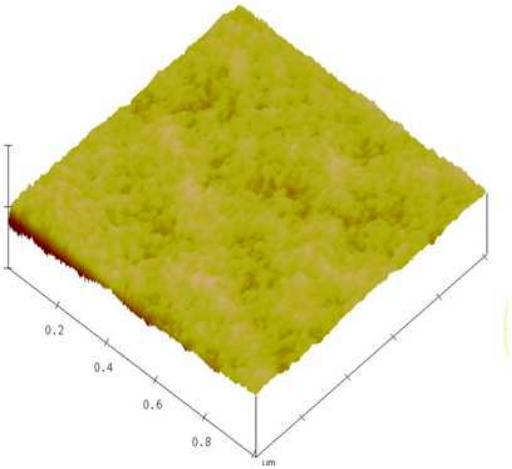
- **Effect of CHP on a-C studied for a contact time of 15 minutes**
- **Blanket a-C surface is smooth with RMS $_{roughness}$ ~ 0.8nm**
- **CHP treated a-C shows modification of surface with RMS$_{roughness}$ ~ 10nm**

AFM Analysis of High Dose Implanted PR film

AFM Contact mode







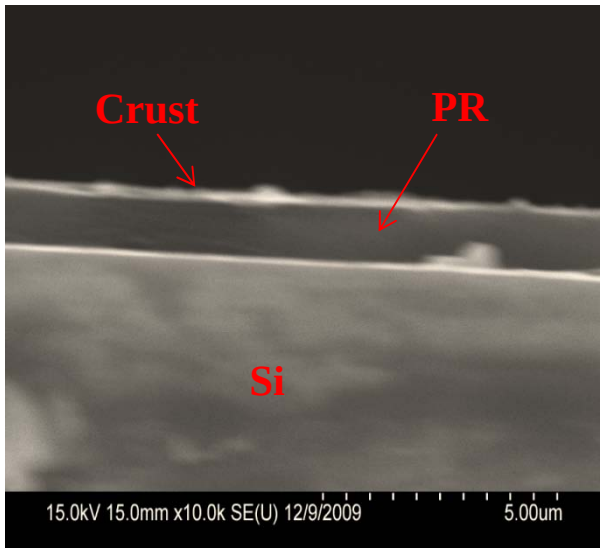
Pile up of removed PR?

Blanket PR 1E16 As/cm^2

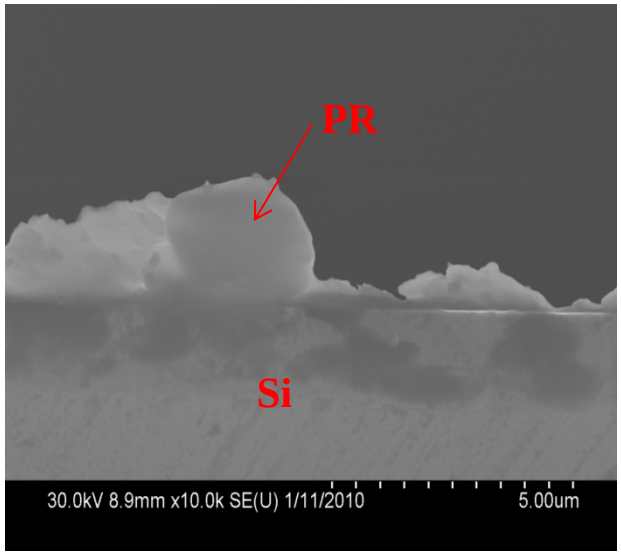
PR 1E16 As/cm^2 in 5mM Fe^{2+}, 20%H_2O_2

- **Effect of CHP on 1E16 As/cm^2 implanted PR studied for a contact time of 15 minutes**
- **Blanket PR surface is smooth with RMS ~ 0.2 nm**
- **CHP treated PR shows disruption on surface with RMS ~ 8 nm**

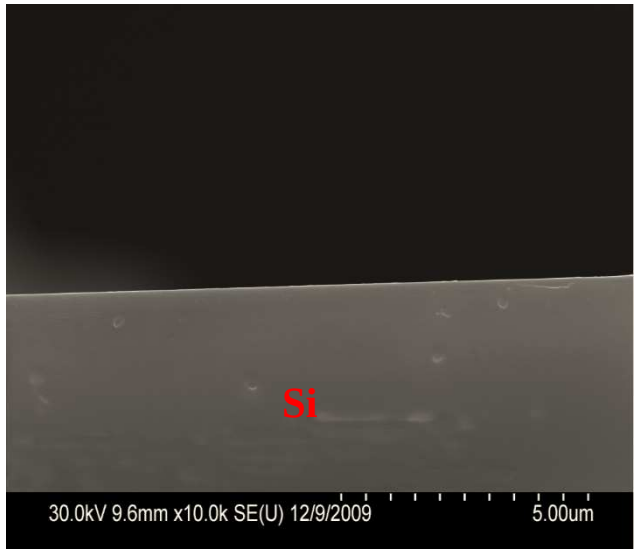
Effect of CHP on High Dose Implanted PR film



Blanket PR



PR in 2:1 SPM



PR in CHP + SPM

- 1E16 As/cm^2 implanted PR shows crust layer
- Discontinuous PR residue film observed after 2:1 SPM treatment for 5 minutes at 80^{0}C
- CHP (5mM Fe^{II}, 20% H_2O_2 ; Time: 30min; room temperature) treated PR was completely removed in 2:1 SPM @ 80^{0}C in 5minutes

Summary

- **Effectiveness of Catalyzed Hydrogen Peroxide system in disrupting crust layer was investigated using a-C film as model compound**

- **Disruption of a-C film surface was observed in CHP system containing 5mM Fe^{II} , 20% H_2O_2 at room temperature**

- **Confocal microscopy has revealed surface disruption with depth ~90 nm and ~300 nm for a-C film and high dose implanted PR respectively**

- ***Complete removal of high dose implanted PR is possible by first exposing the resist in CHP solution for 30 minutes and then in 2:1 SPM at 80^0C for 5minutes***

Future Plans

Next Year Plans

- **Optimization of CHP system to decrease the exposure time prior to conventional SPM treatment**
  - **Variables: H_2O_2/Metal ion level, Time, Temperature, pH**
- **Measure metal levels after cleaning**
- **Work with a tool maker to test the chemical system on full wafers**

Long Term Plans

- **Development of CHP system for one step removal of implanted photoresists**

Industrial Interactions and Technology Transfer

- **Technical discussions with Joel Barnett of Sematech and Hsi-An Kwong of Freescale**

- **Interactions with Dr. Renhe Jia and Dr. Chiu Chan of Applied Materials to decide on a-C films as model films**