April 2002 CMPUG Meeting

Post CMP Cleaning for STI Ceria Slurries

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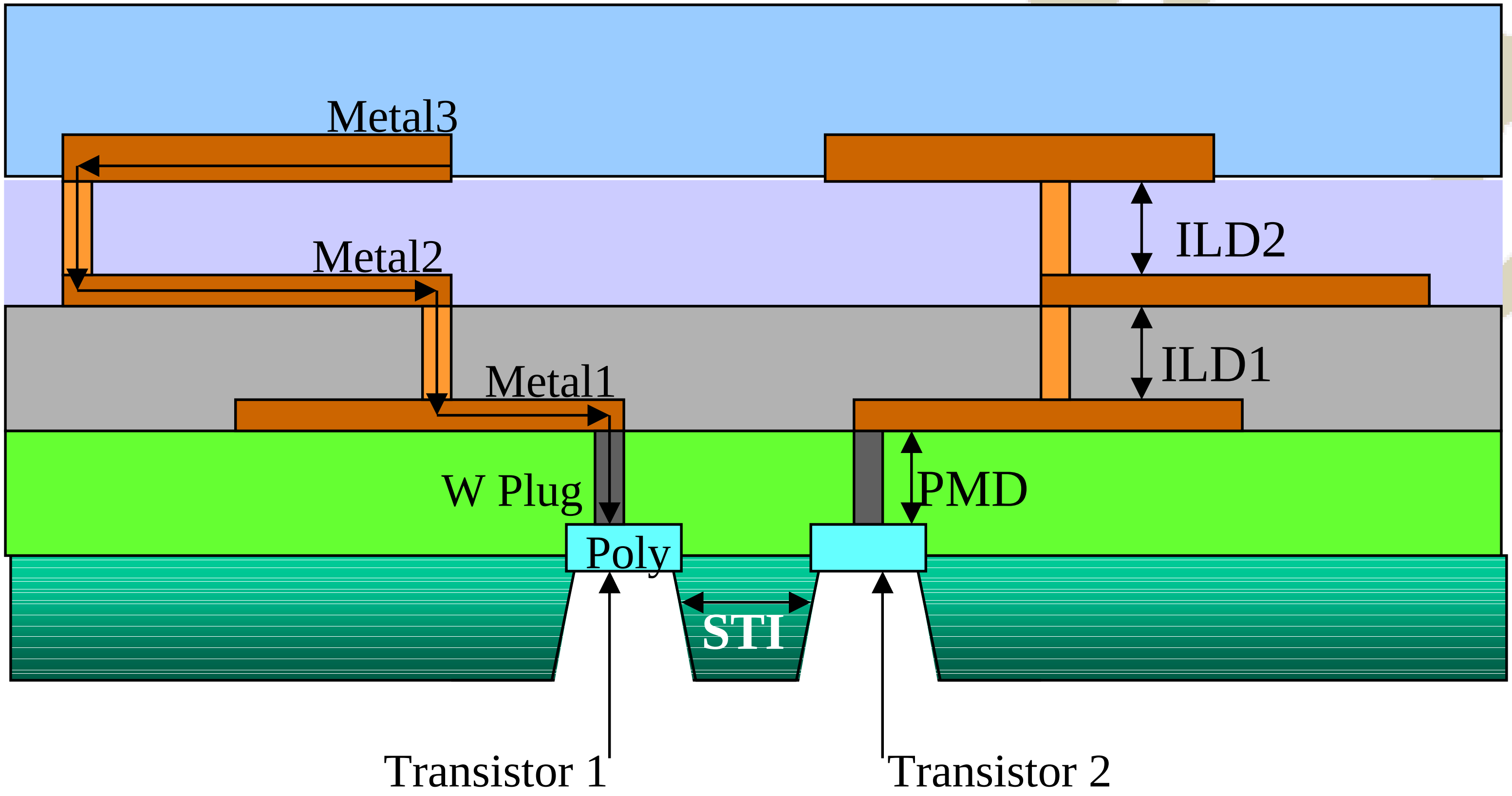
Presentation Agenda

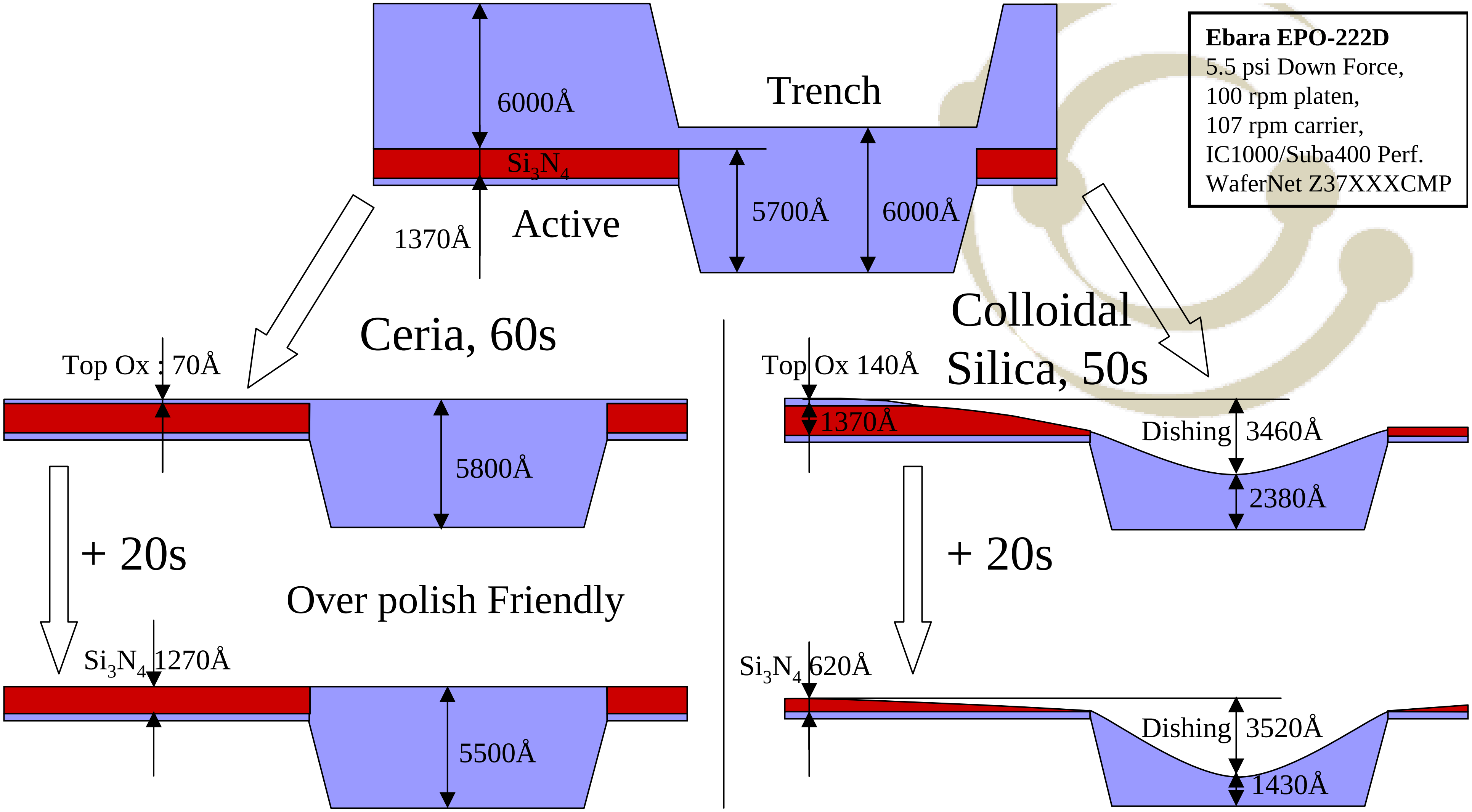
- The STI (shallow trench isolation) CMP process
- Metal ion absorption versus pH
- Ceria chemistry
- Hydrogen peroxide chemistry
- Pourbaix diagram for the Ceria/water system
- Cleaning process parameters
  - ➢ Chemical process time
  - ➢ DI rinse time
- Surface contamination results for metal and ceria ions
- Particle binding forces and removal mechanisms
- Preliminary defectivity results
- Conclusions

STI, PMD and ILD Structures

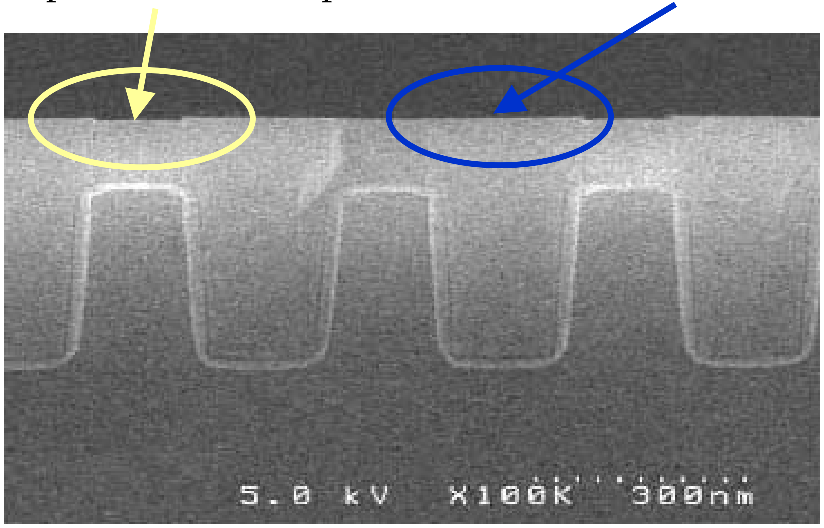


Comparison of Characteristics
Ceria and Silica Slurries

Ebara EPO-222D
5.5 psi Down Force,
100 rpm platen,
107 rpm carrier,
IC1000/Suba400 Perf.
WaferNet Z37XXXCMP

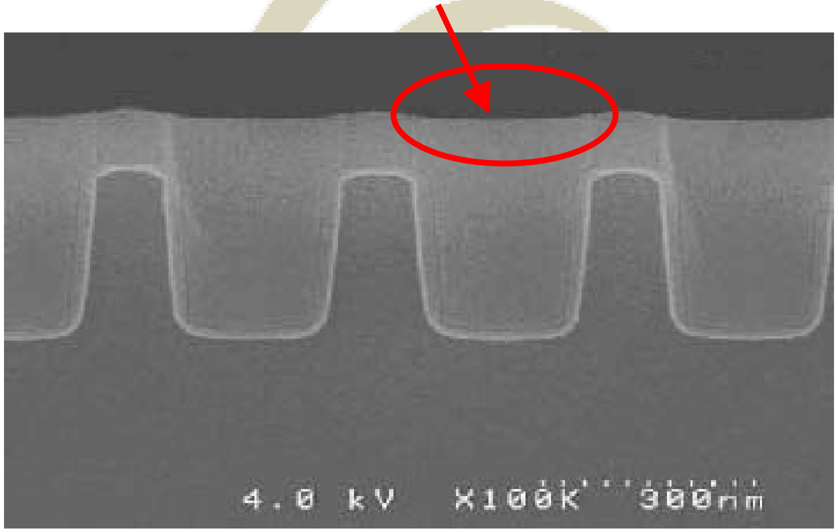


Ceria Surface Finish and Planarity


Phosphoric Acid Strip

Note Excellent Selectivity

CMP2100^{TM} : Flat Surface

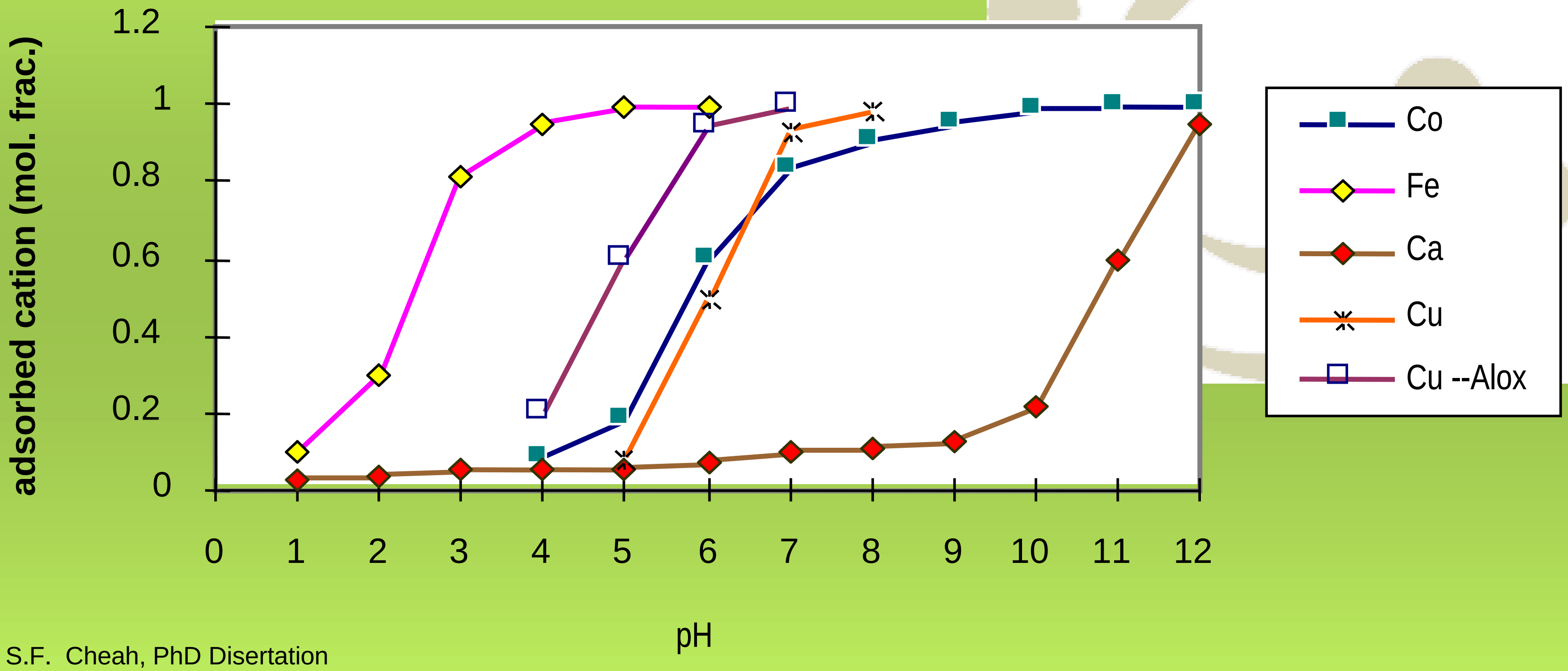

Current Art Typical STI Slurry Dishing

Typical STI Slurry : Dishing Result

1/1 Selectivity Nitride/TOX with CMP2100 On Blanket Wafers
Rate for TOX = 210Å/min ; Si_3N_4=230Å/min.

Process EBARA EPO-222D: 5.5psi downforce, 100 rpm platen, 107 rpm carrier, IC1000/Suba 400 perf.

Absorption of Trace Metals vs pH on Silicon Oxide



1. S.F. Cheah, PhD Disertation

2. K.B. Agashe, et al; J. Colliod & Inter. Sci.; 185, p174 (1997)

Cerium Chemistry

CeO_2 has a long history for polishing optics

Cerium species may "bind" with SiO_2 substrates.

Cerium is the only +4 lanthanide stable enough to exist in aqueous and solid compounds.

$Ce(OH)_3$ and other oxy-acids are normally not soluble in strong acid or alkalies unless there is an oxidizer (H_2O_2, Sn^{+2}, etc) to generate Ce+4.

$Ce^{+4} + nH_2O \dashrightarrow [Ce(H_2O)_n]^{+4}$ (a strong acid)

the anion can polymerize

Oxidation potential is dependent on the acidic medium

$Ce^{+3} \dashrightarrow Ce^{+4} + e^{--}$

Eo = -1.70 ($HClO_4$), -1.61(HNO_3), -1.44(H_2SO_4), -1.28(HCl)

Cotton & Wilkinson, Adv. Inorg. Chemistry

H_2O_2 Chemistry

General oxidation reaction:

$2H_2O_2$ -----> $2H_2O$ + O_2

Hydrogen Peroxide is a weak acid:

H_2O_2 -----> H^+ + HO_2^{--} K= $1.5X10^{-12}$

Redox Potentials:

H_2O_2 + $2H^+$ + $2e^{--}$ ---> $2H_2O$ $E_o = 1.77$ volts

HO_2^{--} + H_2O + $2e^{--}$ ---> $3OH^{--}$ $E_o = 0.87$

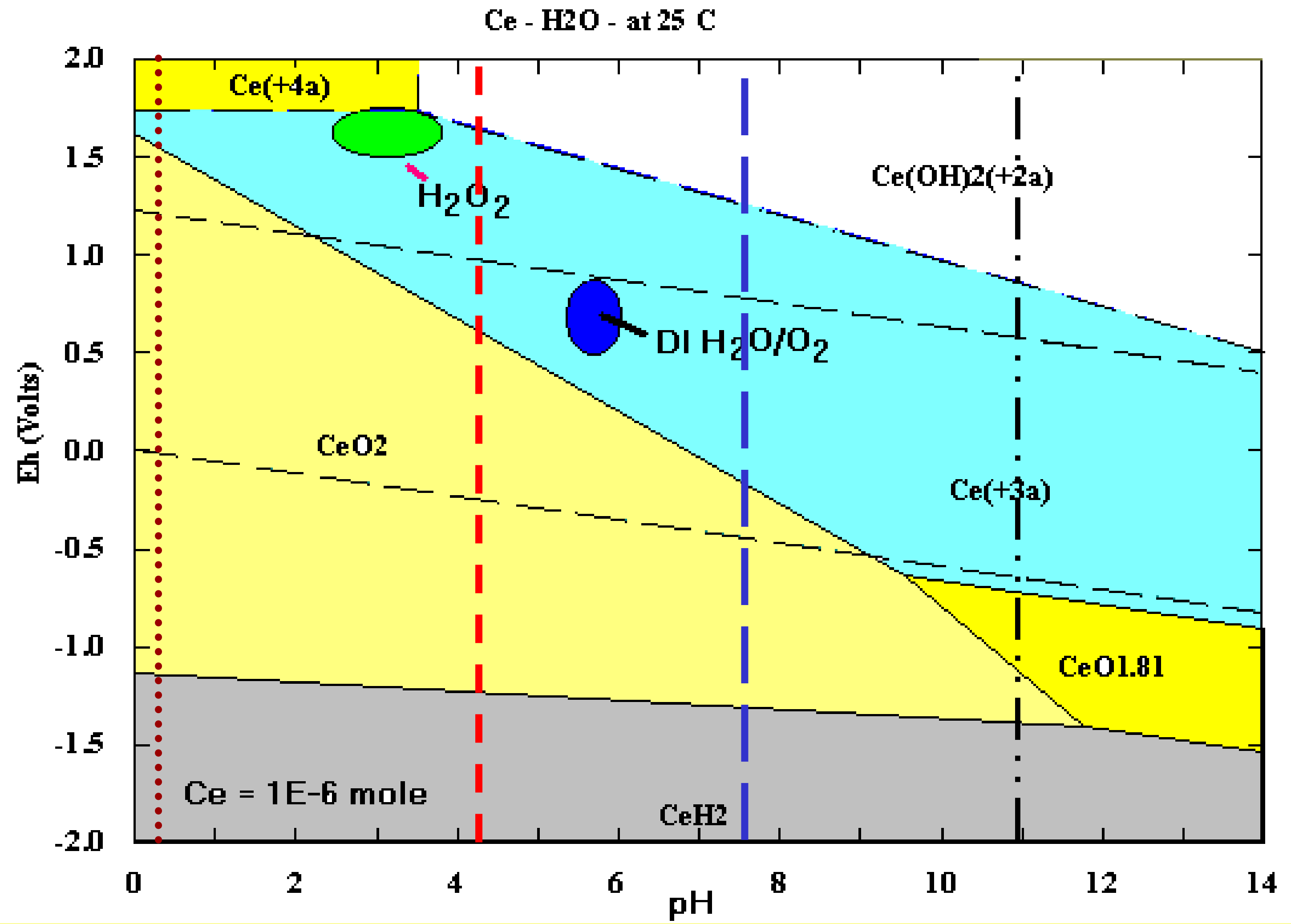
O_2 + $2H^+$ + $2e^{--}$ ---> H_2O_2 $E_o = 0.68$

The catalytic decomposition (Fe^{+3}, Ce^{+4}, I_2, etc.) in:

$H_2\mathbf{O_2}$ + $2Fe^{+3}$ -----> $2Fe^{+2}$ + $\mathbf{O_2}$ + $2H^+$

The oxygen O**--**O bond does not break.

Ceria Pourbaix Diagram



SSEC Single Wafer Cleaner

Typical Process				
1.	30 sec.	DI water	Spray	100 rpm
2.	60 sec.	Chemistry	Brush F	
3.	30 sec.	DI water	Spray	500 rpm
4.	60 sec.	Chemistry	Brush R	
5.	~50 sec.	Chemistry	Megasonic	10 rpm
6.	60 sec.	DI water	Spray	20-100 rpm
7.	30 sec.	Dry		100-1500 rpm

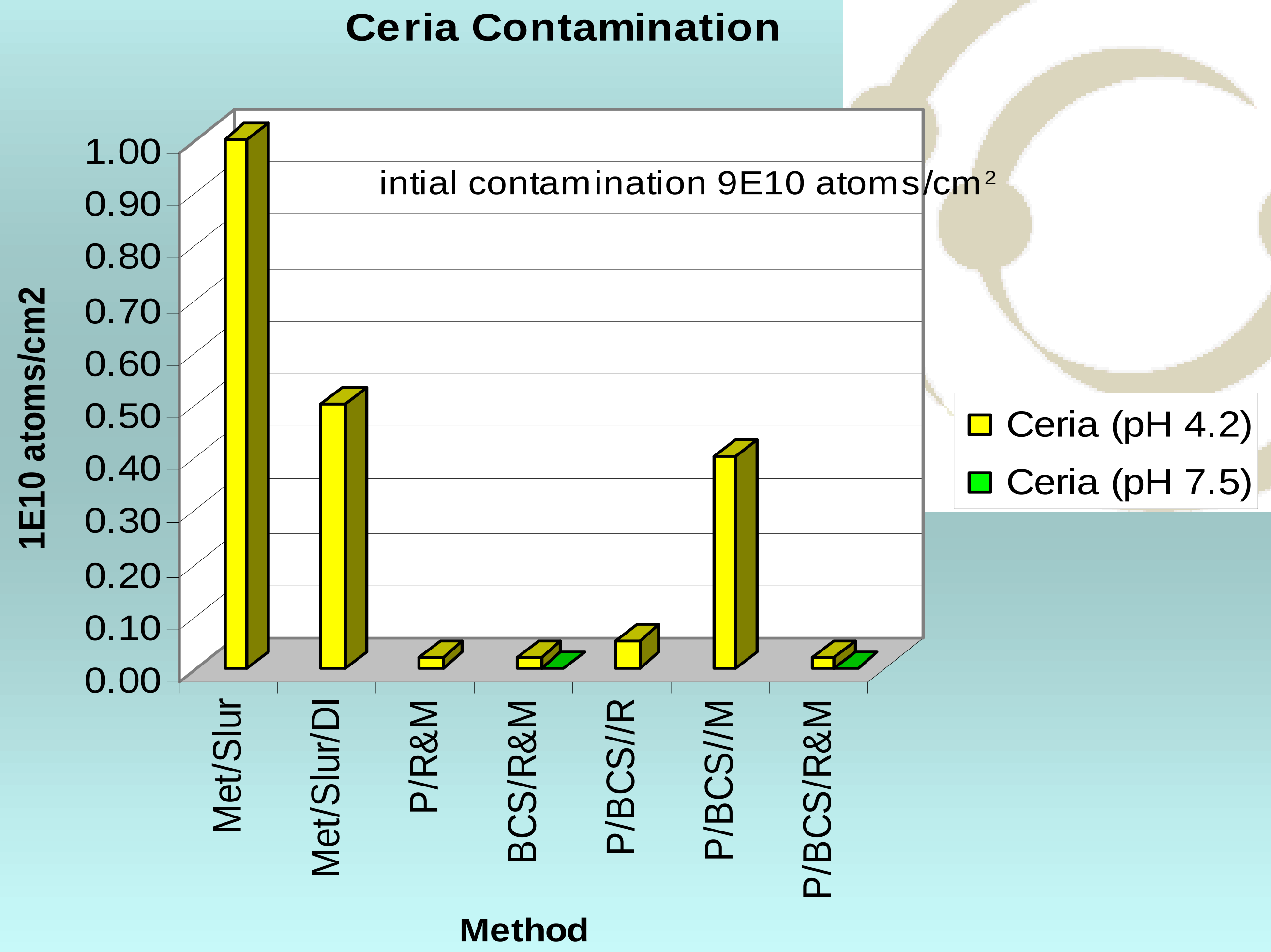
Process at 25 C

Surface Contamination (VPD-ICP-MS)

	Method	Ca	K	Na	Fe	Cr	Ni	Zn	Mg	Cu	Ce
1	Control 1	26.0	1.0	4.7	0.4	*	*	3.5	2.6	2.5	*
2	Control 1 (H_2O_2/BCS)	1.5	*	0.9	*	*	0.1	1.9	1.2	1.7	*
3	Control 2 (Metal)	12.0	10.0	18.0	480.0	1.1	0.7	3.9	49.0	8.7	0.9
4	***Control 3 (Met/Slur)***	***10.0***	***4.0***	***7.2***	***260.0***	***0.3***	***0.6***	***15.0***	***30.0***	***2.8***	***9.0***
5	Control 3 and DI	2.1	1.5	1.4	220.0	*	0.2	8.8	7.1	3.3	0.5
6	H_2O_2//Roll&Meg	1.4	2.0	2.1	110.0	*	1.1	3.6	5.3	4.1	0.02
7	BCS//Roll&Meg	0.7	1.2	0.8	68.0	*	0.3	3.3	3.5	2.4	0.02
8	H_2O_2/R//BCS/M	1.7	160	2.9	97.0	0.1	0.3	3.8	7.4	2.9	0.09
9	BCS/R//H_2O_2/M	5.4	6.1	3.5	140.0	0.3	0.6	6.0	11.0	4.2	0.10
10	BCS/H_2O_2//Roller	0.9	2.1	1.3	88.0	*	0.1	2.6	4.0	2.5	0.05
11	BCS/H_2O_2//Meg	1.0	2.6	1.8	79.0	0.6	0.5	2.8	12.0	2.8	0.40
12	BCS/H_2O_2//R-M	**0.9**	**2.4**	**0.9**	**55.0**	*****	*****	**1.7**	**3.6**	**1.6**	**0.02**
	* Detection Limit	0.5	0.5	0.5	0.1	0.05	0.1	0.2	0.2	0.1	0.01
	1E10 atoms/cm2		R= rollers			M=1.25 MHz megasonics					

Balazs Analytical TEOS films BCS pH=4.2

Ceria Contamination Results

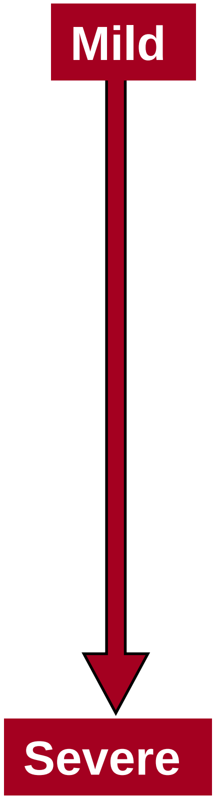


Particle Binding Forces

- Particle size
  - ➢Several factors complicate relationship
- Electrostatic effects
- Van der Waals forces
- Surface roughness
- Chemical bonding and hydrogen bonding

Particle and Impurity Removal Mechanism

Mechanism for removing impurities for wafers(1)


Mild

Severe

- ➢ *Physical* - replacing strongly absorbed particles with a large volume of weakly absorbed solvent.
  - Mechanical
  - Ultrasonic / megasonic
- ➢ *Surface charge*- use acids or bases or surfactants to effect the Si-OH or M-OH groups.
- ➢ *Ion exchange*- removing metal ions by adding acids.
- ➢ *Redox* of impurities - change the oxidation state or decompose the impurity.
- ➢ *Etching the surface* - the surface is etched (dissolved) to undercut the impurity.

(1) SPWCC, March 4, 1996

Preliminary Defectivity Results with BCS (pH 7.5)

Wafer #	LPD's	Conditions
1	N/A	Metal dip only
2	55699	Metal and slurry dip only
3	940	M/S dip, perox./R & M, DI water
4	21434	M/S dip, BCS (pH 7.5) R & M AH, DI water
5	128	M/S dip, BCS (pH 7.5) perox, R & M AH, DI water
6	105	M/S dip, BCS (7.5) perox, R & M no AH, DI
7	716	M/S dip, BCS (7.5) perox, R & M no AH, DI [OP]
8	1434	Reducing acid, AH, DI water
SP 1 @ 0.17um		

TEOS wafers

Preliminary Defectivity Results with various cleaning solution

	Methods	**pH**	**LPD**
1	Control 1		647
2	Control 2 (Metal)	~6	>70000
3	***Control 3 (Met/Slur)***	***~6***	>70000
4	Control 3 and DI	~6	7002
5	H2SO4/H2O2	<1	28571
6	EKC5000/H2O2	4.2	2528
7	**LPX-100/H2O2**	**7.5**	**87**
8	EKC5200/H2O2	7.5	1874
9	EKC5100/H2O2	8.5	105

Dipped TEOS wafers

Conclusions

- Ceria slurries are effective for STI.
- BCS solutions (pH 4.2 & 7.5) can reduce ceria ions below 1E8 atoms/cm^2
- Hydrogen peroxide is also effective for removing metal ions.
- Preliminary results show that defects can be reduced with BCS or BCS and Peroxide

  (pH 4.2 or 7.5)
- More work is in progress at other pH conditions.

Acknowledgements

We would like to thank:

- Pascal Berar EKC KK
- Nojo Haruki EKC KK
- Ron Jee EKC Inc.
- Cass Shang EKC Inc.
- Solid State Equipment Co.