April 2002 CMPUG Meeting

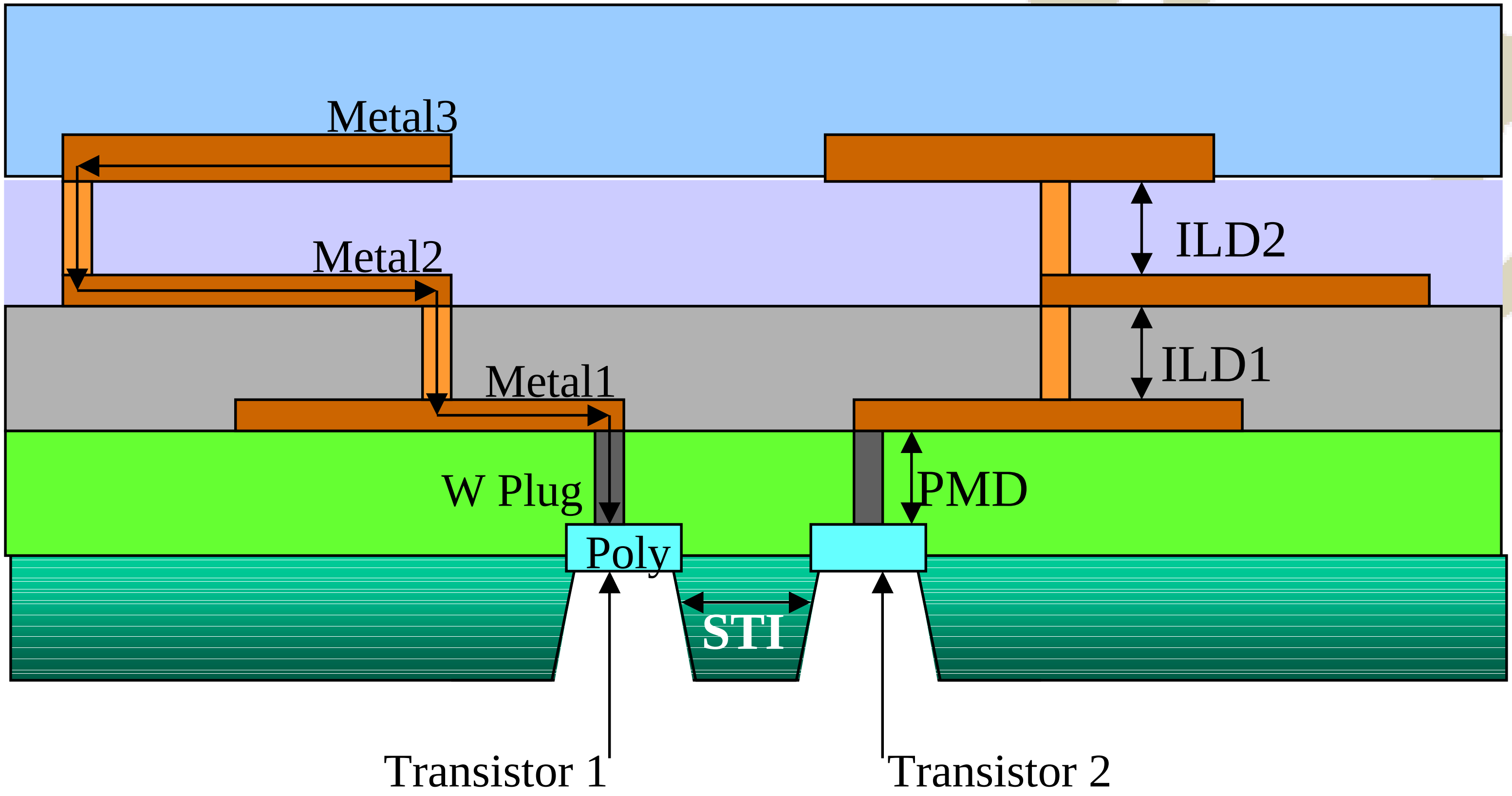
Post CMP Cleaning for STI Ceria Slurries

Robert Small, Ph.D., Brandon Scott
EKC Technology, Inc.
Hayward, CA

Presentation Agenda

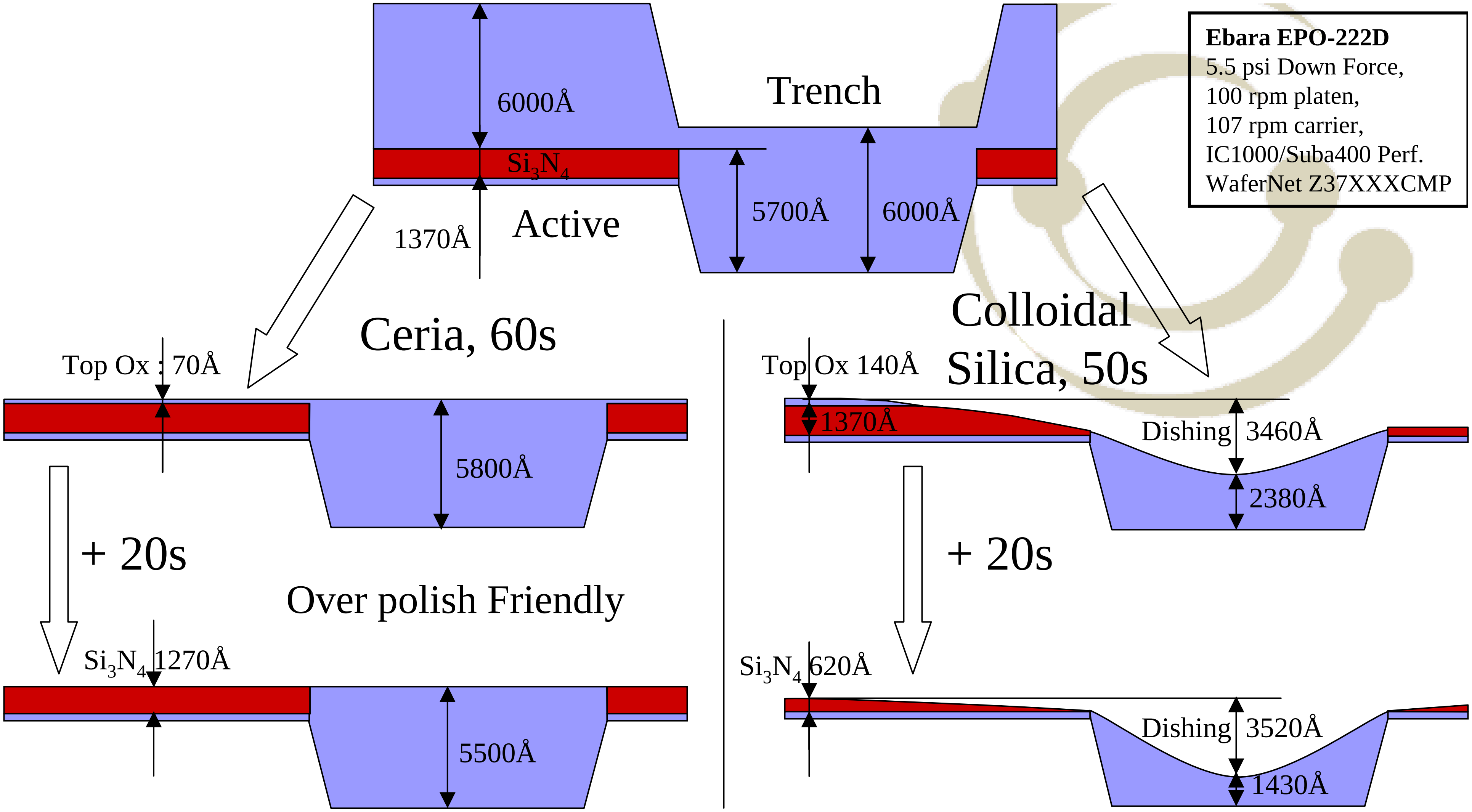
- The STI (shallow trench isolation) CMP process
- Metal ion absorption versus pH
- Ceria chemistry
- Hydrogen peroxide chemistry
- Pourbaix diagram for the Ceria/water system
- Cleaning process parameters
  - ➢ Chemical process time
  - ➢ DI rinse time
- Surface contamination results for metal and ceria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

STI, PMD and ILD Structures

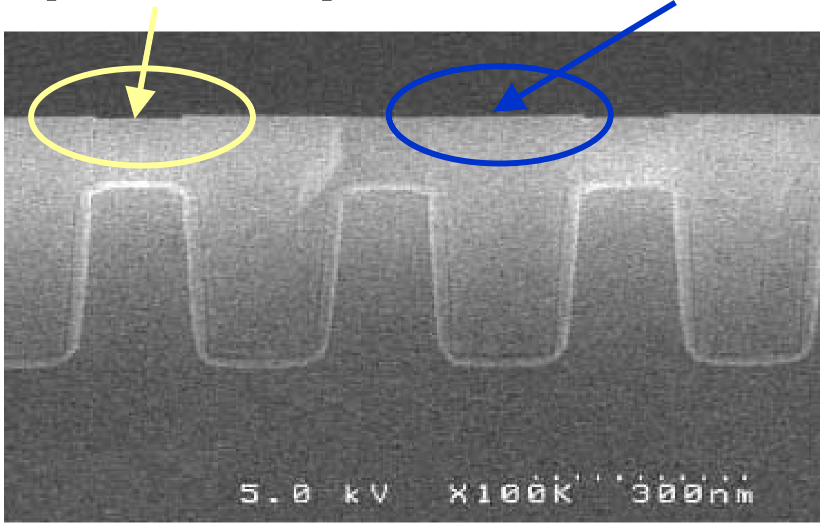


Comparison of Characteristics Ceria and Silica Slurries

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

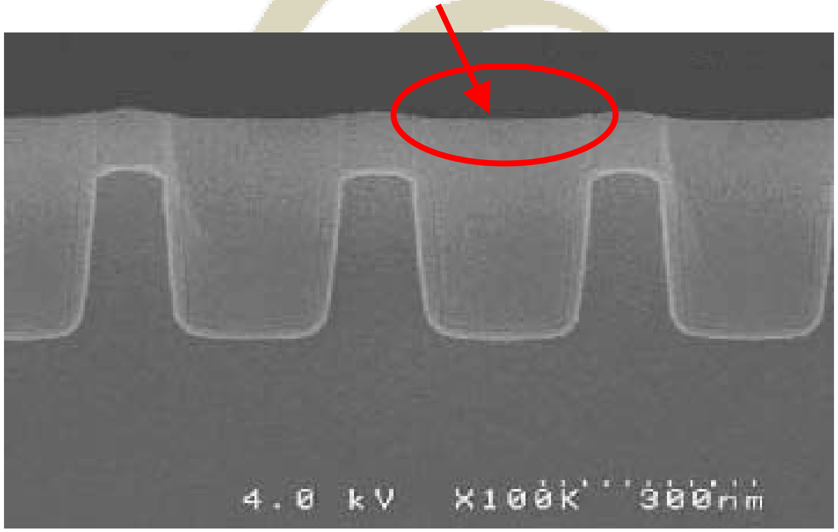


Ceria Surface Finish and Planarity


Phosphoric Acid Strip

Note Excellent Selectivity

CMP2100^{TM} : Flat Surface

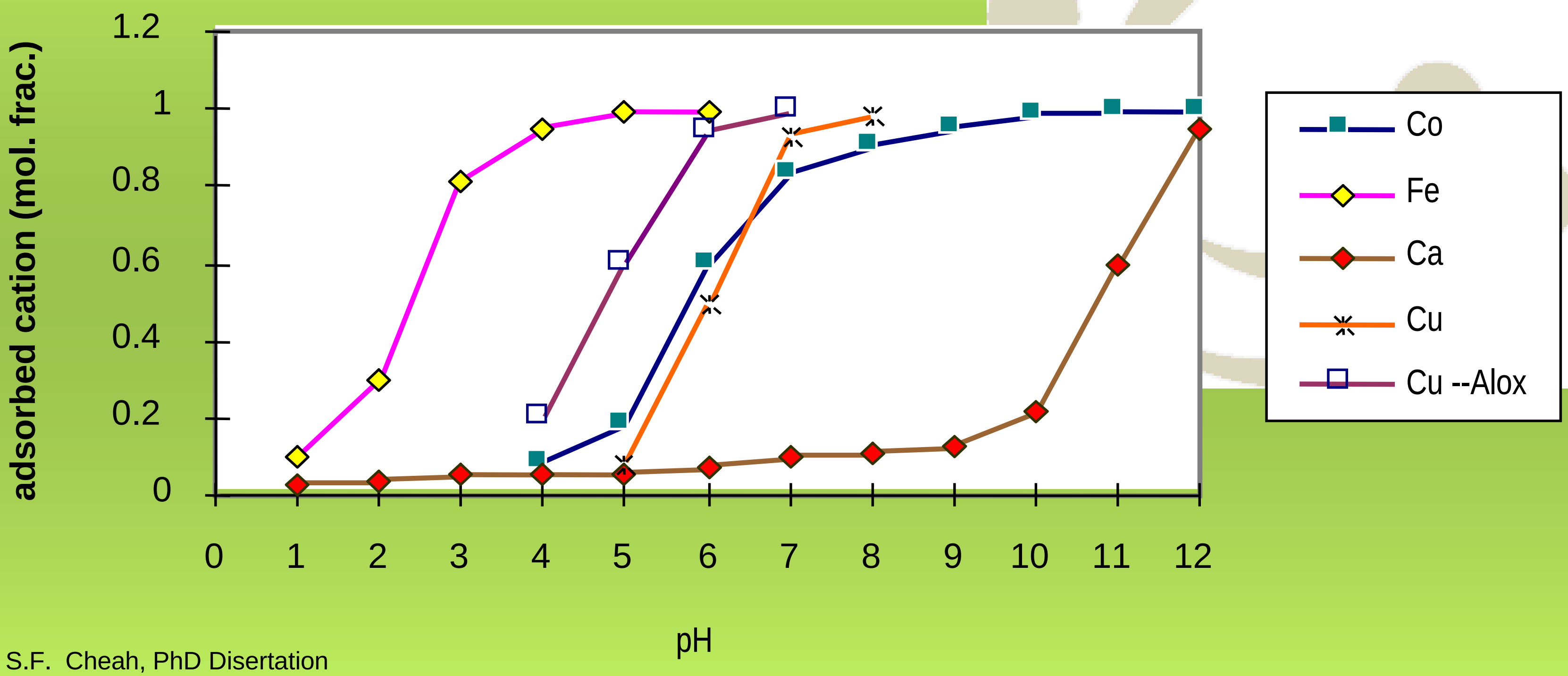

Current Art Typical STI Slurry Dishing

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

$Ce^{+3} \text{ ----> } Ce^{+4} + e^{--}$

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= $1.5X10^{\mathbf{-12}}$

Redox Potentials:

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

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

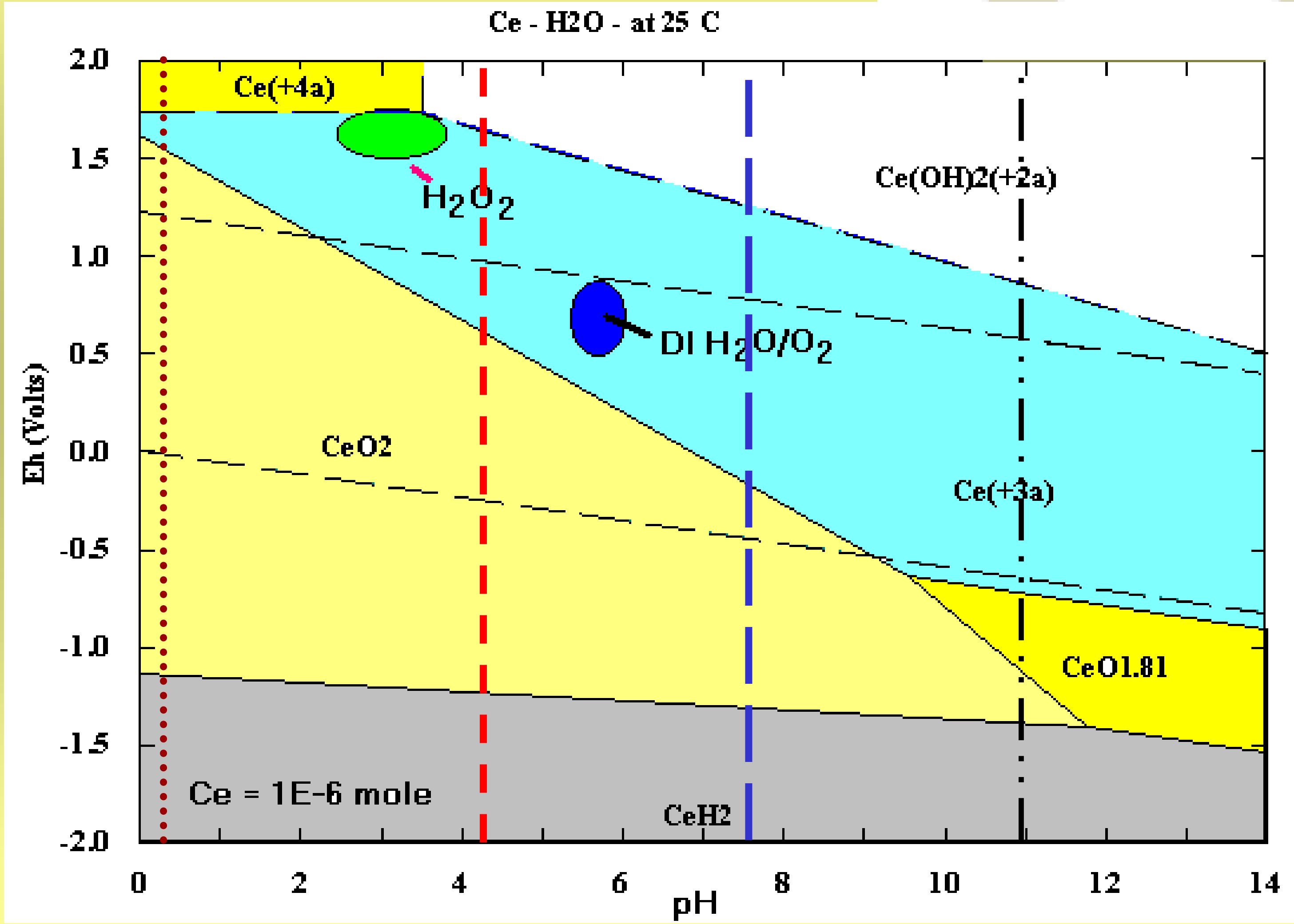
O_2 + $2H^+$ + $2e^{--}$ ---> H_2O_2 E_o = 0.68

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

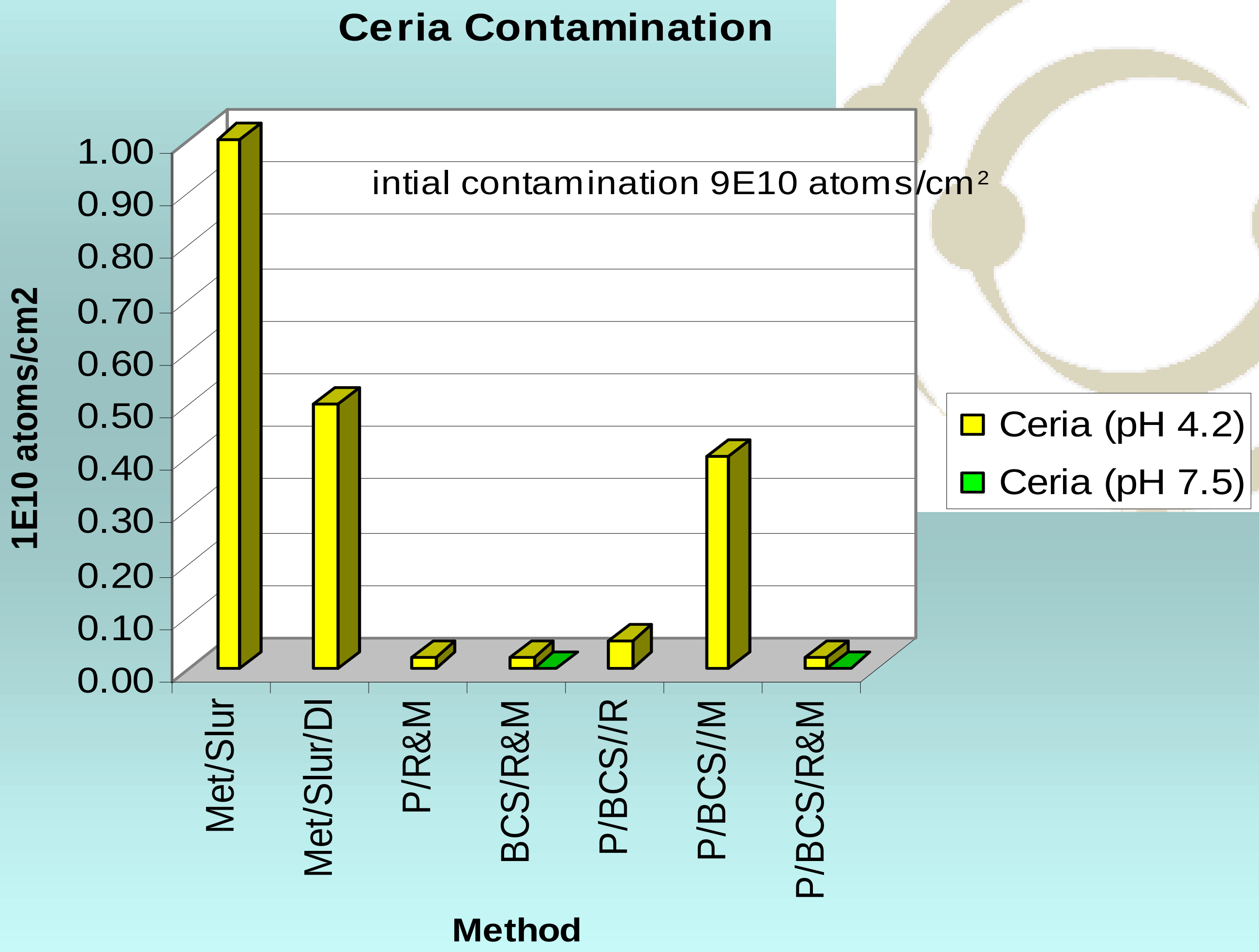
Process at 25 C

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 (H2O2/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	H2O2//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	H2O2/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//H2O2/M	5.4	6.1	3.5	140.0	0.3	0.6	6.0	11.0	4.2	0.10
10	BCS/H2O2//Roller	0.9	2.1	1.3	88.0	*	0.1	2.6	4.0	2.5	0.05
11	BCS/H2O2//Meg	1.0	2.6	1.8	79.0	0.6	0.5	2.8	12.0	2.8	0.40
12	BCS/H2O2//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

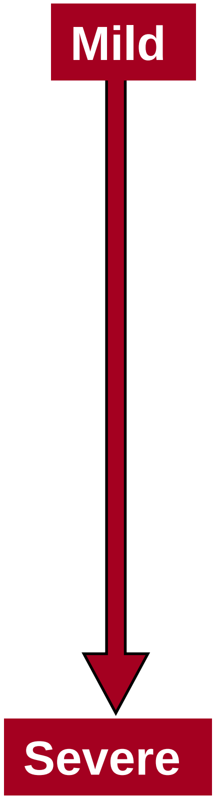


Particle Binding Forces

- 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)



- ➢ *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.