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Post CMP Cleaning for Copper, STI and Tungsten

Presentation Agenda

- **Post CMP Process Background**

  Market

  Mechanisms

  BCS - Buffered Chelating Solutions

- **Post CMP after STI CMP**
- **Post CMP after W CMP**
- **Post CMP after Cu CMP**
- **Conclusion**

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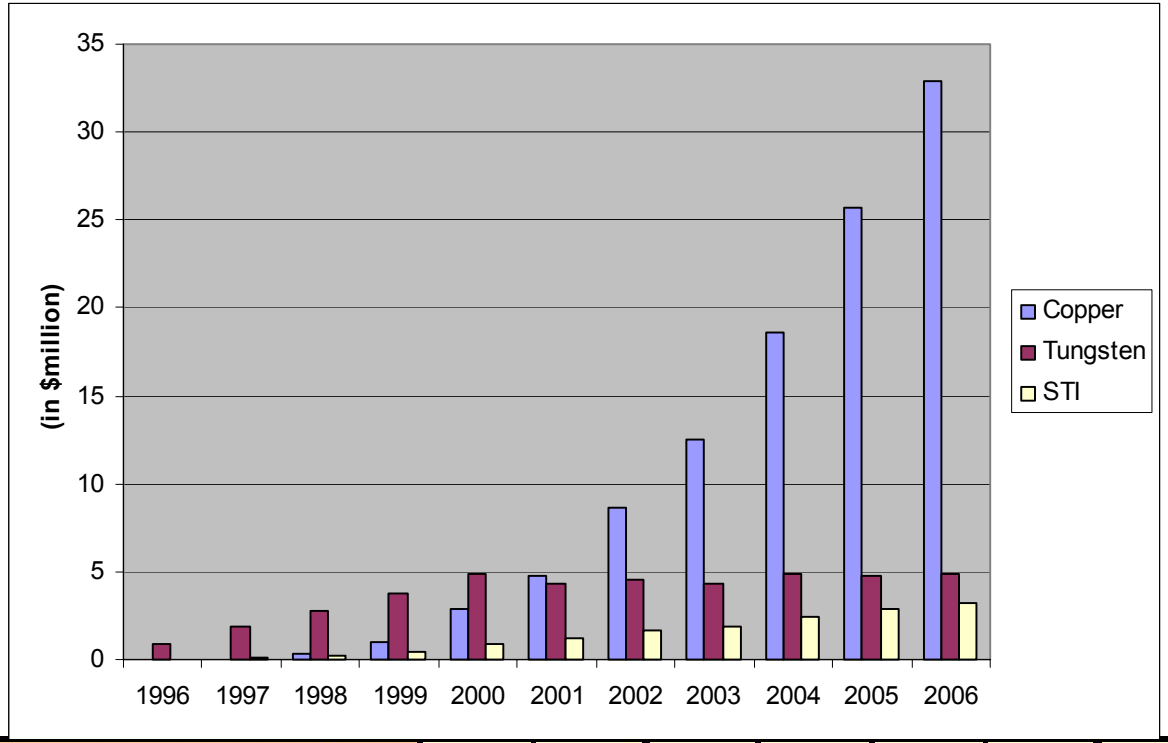
Post CMP Cleaning Process Background

Market projection for PCMP Cleaning Chemicals



Source: Laredo Technology

Post-CMP Cleaning Chemical Market, $ Millions	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Copper ($0.10/wafer)	0.00	0.00	0.34	0.97	2.89	4.72	8.63	12.49	18.61	25.70	32.88
Aluminum ($0.05/wafer)	0.00	0.00	0.00	0.00	0.00	0.39	0.81	1.25	1.86	2.57	2.90
Tungsten ($0.05/wafer)	0.86	1.90	2.81	3.75	4.88	4.33	4.59	4.37	4.84	4.71	4.84
Poly ($.03/wafer)	0.00	0.00	0.10	0.36	0.65	0.94	1.46	1.87	2.46	3.08	3.48
STI ($.03/wafer)	0.03	0.13	0.26	0.44	0.87	1.18	1.62	1.87	2.46	2.83	3.19
PMD/ILD ($.03/wafer)	1.17	1.99	2.96	3.92	5.53	5.43	7.28	7.87	7.81	7.71	7.83
Total Market, $ Millions	2.06	4.02	6.47	9.43	14.83	17.01	24.39	29.73	38.03	46.60	55.13
Weighted Post-CMP Chemical Cost, $/Wafer	0.036	0.037	0.038	0.039	0.041	0.043	0.045	0.048	0.051	0.054	0.057

The Challenges …Now and Ahead

ITRS 2001							
Year of Production	2001	2002	2003	2004	2005	2006	2007
DRAM 1/2 Pitch (mm)	*130*	*115*	*100*	*90*	*80*	*70*	*65*
Water Consumption							
Fab UPW use (gal/300 mm wafer)	~1240		~1060		~630		
Chemical Consumption							
Chemical use			Reduce ~5%/yr.			Reduce ~5%/yr	
Recycle/Reuse							
Waste water recycle rate (%)	60%		65%		70%		

Typical Contaminants for FEOL and BEOL

Typical Contaminants from Wet Cleaning		
Contaminats	**Possible Source**	**Possible Impact**
Sodium	DI H2O, chemicals	Gate oxide integrity
Aluminum	Chemicals	Gate oxide kinetics
Fe, Ni, Cr, Cu	Chemicals	Min. carrier lifetime
Zinc	Chemicals	NFU
Calcium	Chemicals, DI H2O	Gate oxide integrity
Boron	DI H2O, chemicals	Gate oxide integrity
Organics	DI H2O, H2O2	Thin-film grow th, haze
Phosphate	Chemicals	Gate oxide integrity
Fluoride	HF, DI H2O	Gate oxide kinetics
Chloride	HCl	Corrosion
Ammonia	NH4OH	Haze
Sulfate	H2SO4	Haze
Oxygen	DI H2O	Thin-film quality
Particle	Acids, DI H2O	Gate oxide integrity
Bacteria	DI H2O	Paricle-induced defects
Silica	DI H2O	Paricle-induced defects

Semicon. Inter. p. 40, March, 2002

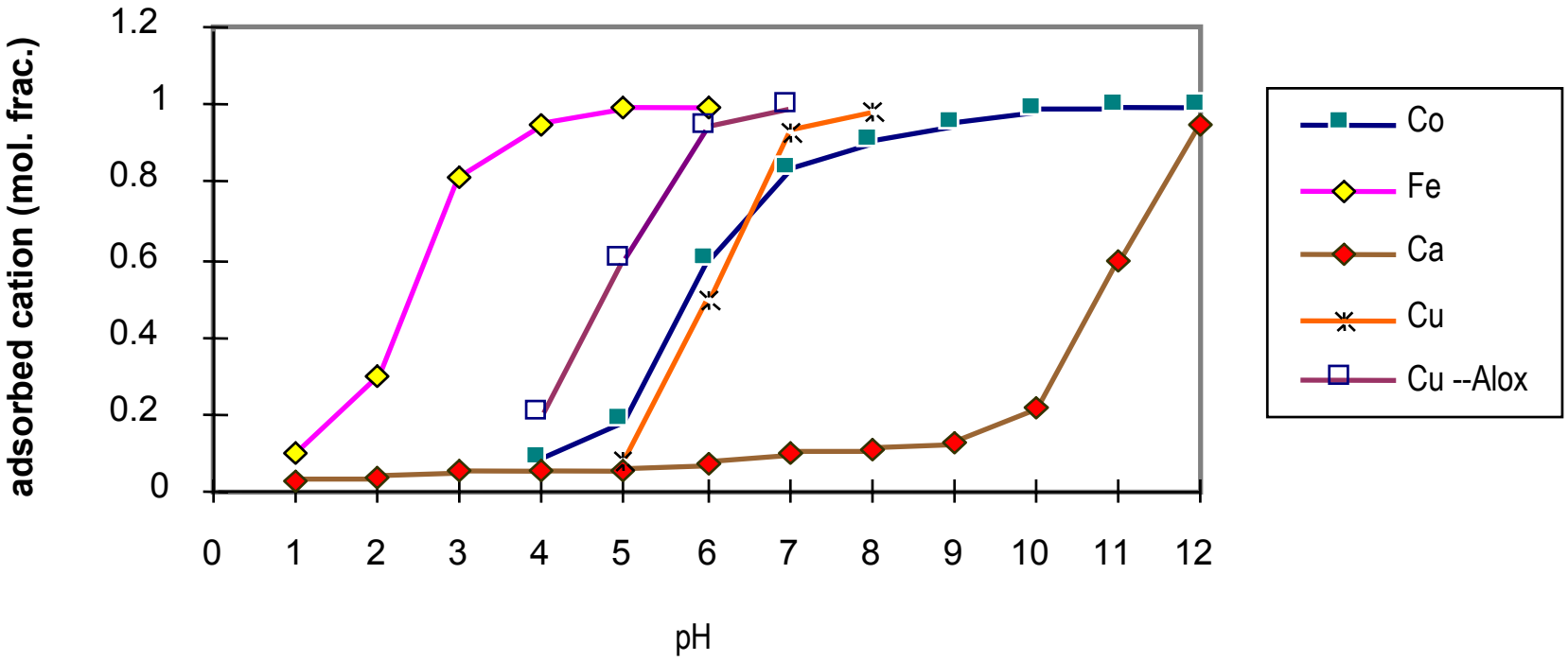
Background on BCS - Buffered Chelating Solutions

Semiconductors manufacturers needed to effectively remove post-etch and post-ash cleaning chemistries without allowing corrosion in the interconnect structure and minimizing surface contamination

- Replacement of IPA - Safety and environmental benefits
- Neutralization of amines - Buffering effect desirable for stability and capacity
- Capture and prevent re-deposit of dissolved species - Chelators can be very effective
- Reduction of rinse water consumption

The principles learned from this application became the basis for similar work in post CMP cleaning

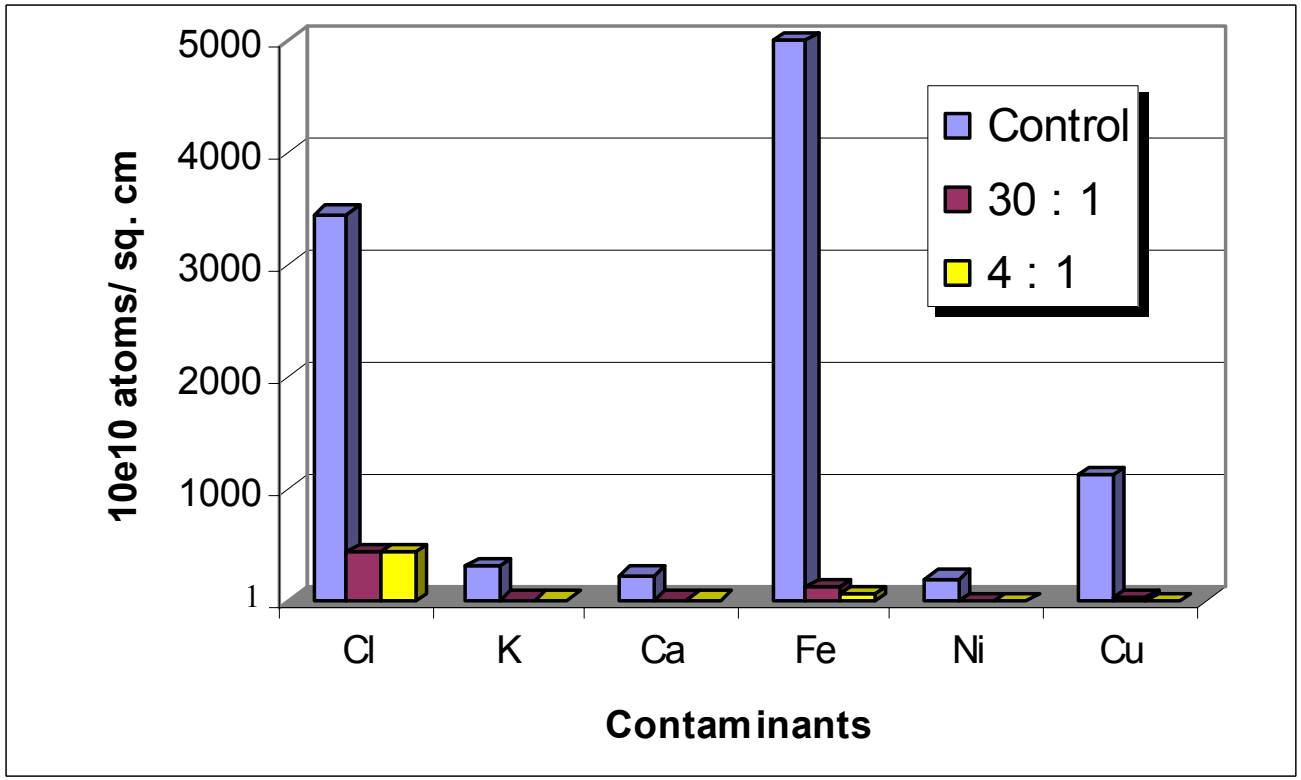
Adsorption of Trace Metals vs pH on Silicon Oxide



1. S.F. Cheah, PhD Disertation

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

TXRF Results Before and After BCS Processes (at pH 4.2)



BCS = PCMP5000™, OnTrak DSS Series 1, 45 sec/brush box.
Chemistry in first brush box only.

Post CMP Requirements

- Excellent throughput
- No negative effects on the device and/or films, including standard and low-k dielectrics
- Reduce surface particles
- Reduce mobile ion contamination
- Eliminate copper dendrite formation
- Reduces DI water consumption
- Low Cost of Ownership
- Environmentally friendly components, with waste stream compatibility

Mechanisms - Particle Binding Forces

Particle size

Adhesion is a function of particle diameter, contact area, surface roughness

Electrostatic effects

Function of zeta potentials and separation distance

Van der Waals forces

Particle removal is determined by the net attraction of van der Waals attraction and electrostatic repulsion

Chemical bonding and hydrogen bonding

Important “forces” for many particles, especially cerium oxide

Particle and Impurity Removal Mechanism

Mechanisms for removing impurities from wafers(1)

Mild

Severe

- *Physical* - displace strongly adsorbed particles with a large volume of weakly adsorbed solvent.
  - Mechanical
  - Ultrasonic / megasonic
- *Surface charge* - use acids, 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

Wafer Cleaning Equipment

Dip Tanks

- Batch process, typically single cassette
- Evolved to include greater control in wafer and chemical handling
- Made more efficient with the addition of ultrasonic and megasonic

Spray Processors

- Cassette
- Single wafer

Brush Cleaners

- Stand alone units
- Modules integrated with polishing tool
- Chemistry limitations, including PVA compatibility

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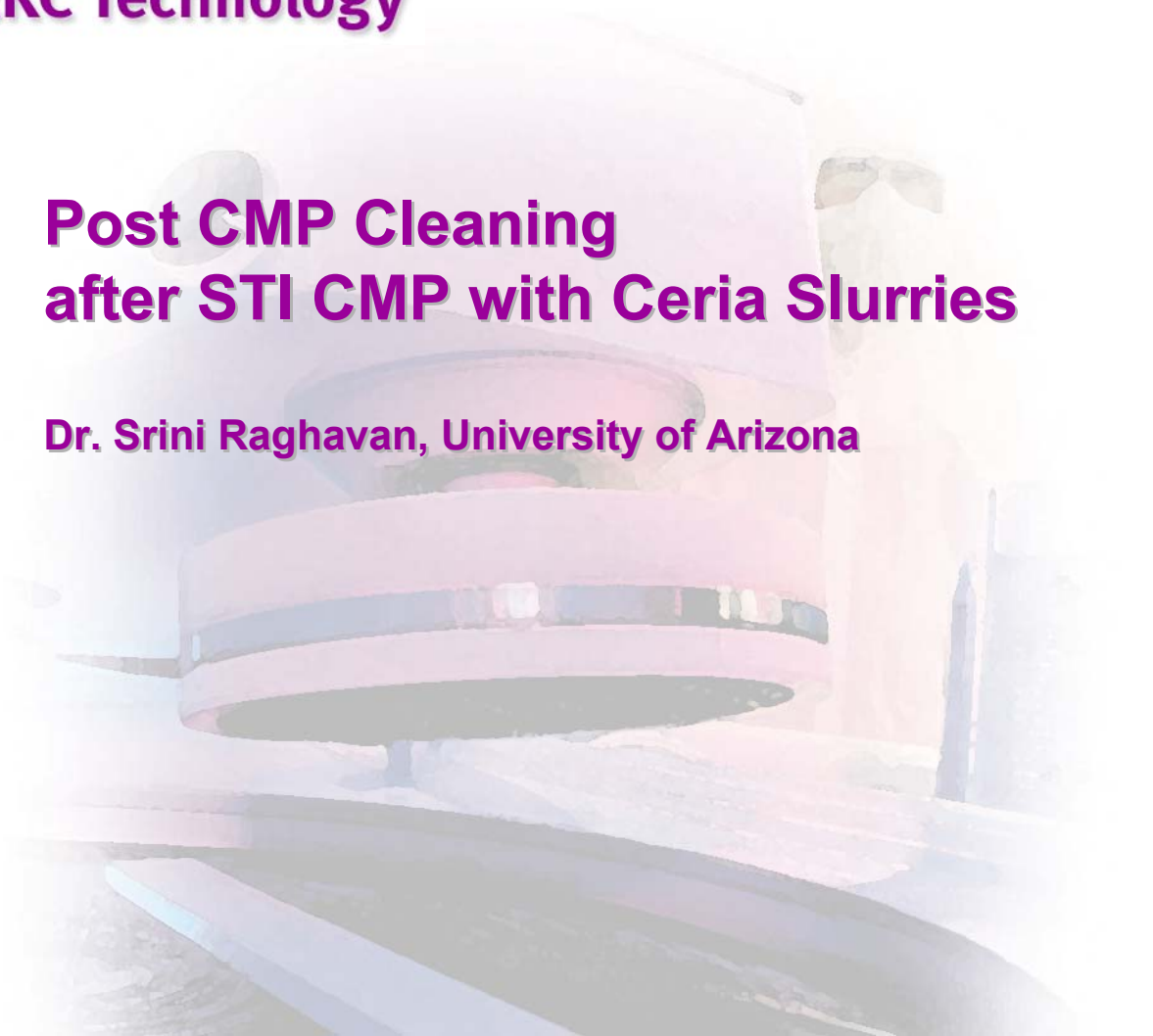
Post CMP Cleaning after STI CMP with Ceria Slurries

Dr. Srini Raghavan, University of Arizona



Background

Ceria based slurries are increasingly used in the CMP of CVD silicon oxide films to obtain STI structures

Unlike silica or alumina, ceria has redox characteristics

Removal of ceria particles from planarized surfaces may be possible using chemical reagents that can participate in redox reactions

Hydroxylamine is a reducing agent –

Is ceria-hydroxylamine reaction possible?

Objectives

Study the dissolution of ceria in hydroxylamine based chemistries

Determine the effectiveness of hydroxylamine based chemistries in removing ceria particles from planarized surfaces

Materials & Methods

Pourbaix diagrams were constructed using STABCAL

Dissolution experiments were carried out in a controlled environment lab scale reactor

Concentration of Cerium was determined by ICPMS

Polishing experiments were carried out on a IPEC472 CMP Polisher

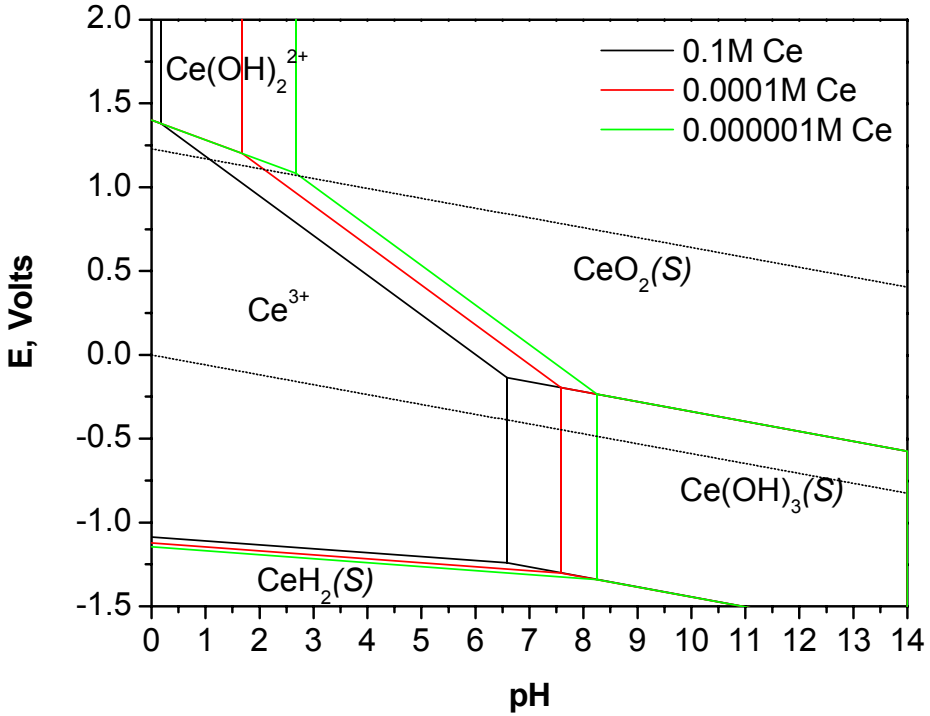
- Pad: IC1000 perforated pad
- Slurry: STI2100 RA3, pH=4.9

Post CMP cleaning tests were performed in a SSEC Megasonic cleaner

Cleaned wafers were scanned using KLA SP1 scanner

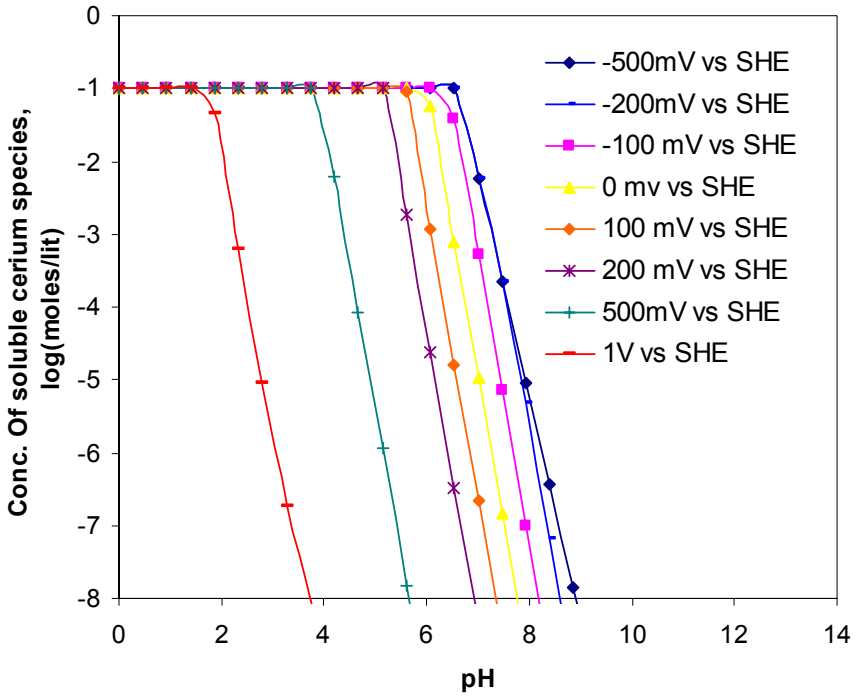
Zeta potential measurements using Delsa 440SX

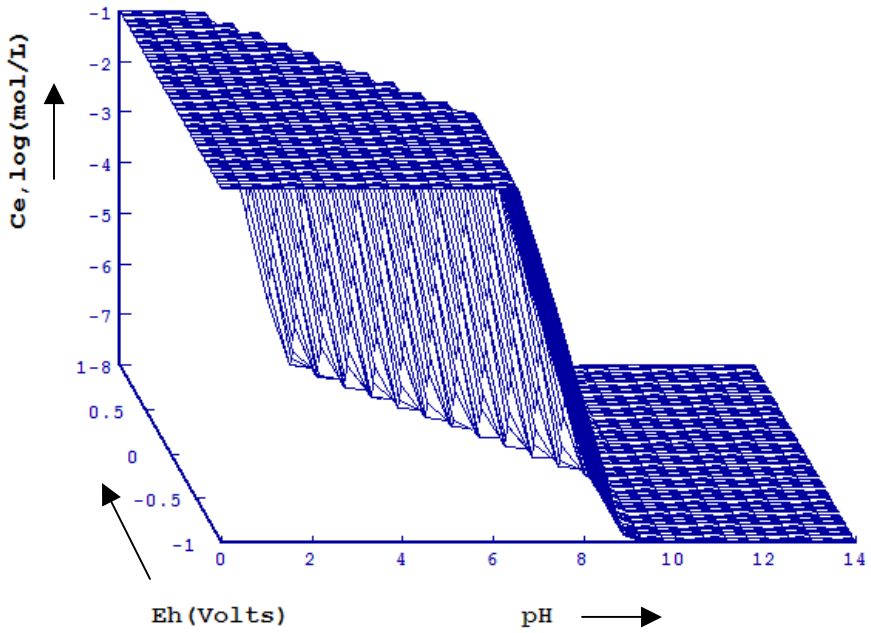
Potential-pH Diagram of Ce-H_2O System



- Solid cerium species: **Ce**, **CeO_2**, Ce_2O_3, **CeH_2** and **Ce(OH)3**
- Aqueous cerium species: Ce^{2+}, **Ce^{3+}**, Ce^{4+}, $CeOH^{3+}$, **$Ce(OH)_2^{2+}$**, $Ce_2(OH)_3^{5+}$, $Ce_2(OH)_4^{4+}$, $Ce_3(OH)_5^{4+}$ and $Ce_6(OH)_{12}^{12+}$

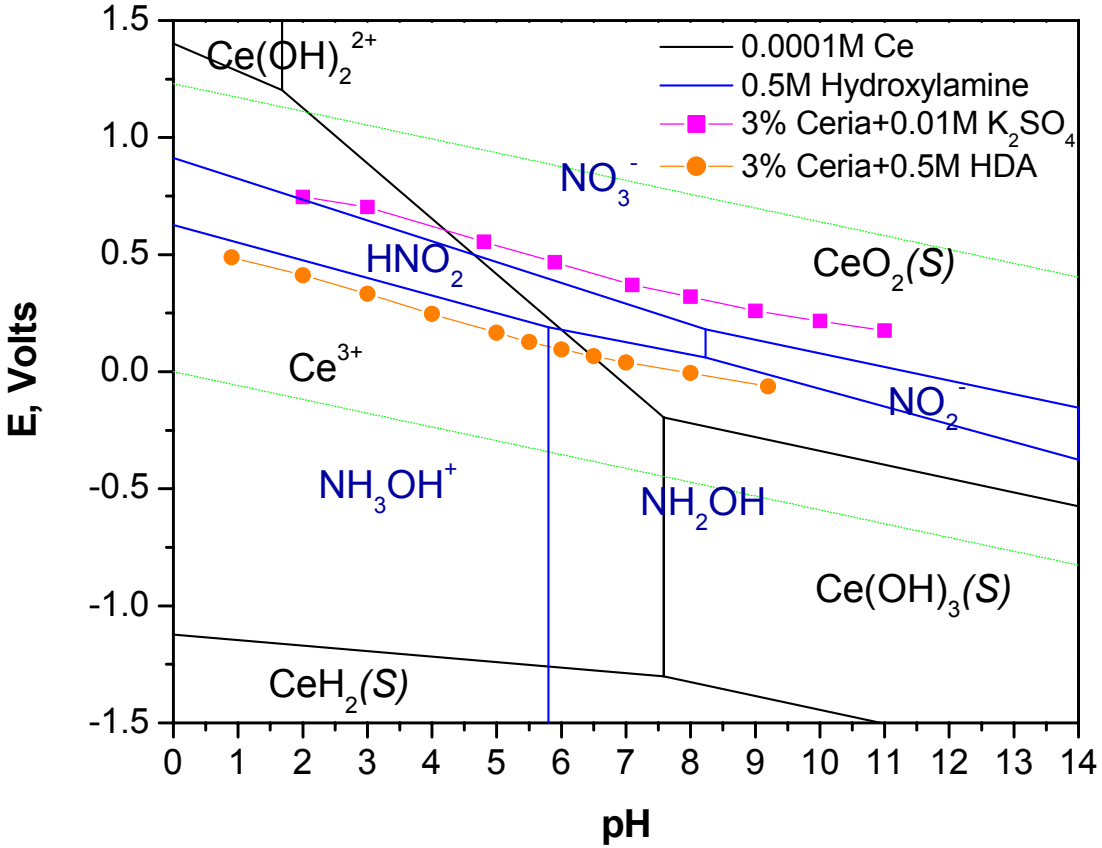
Predicted Solubility of Ceria in Water





- Based on total cerium concentration of 0.1 mol/lit
- The solubility range (pH conditions) of Ceria can be enhanced by lowering the redox potential of the solution.

Redox Behavior of Ceria-Hydroxylamine

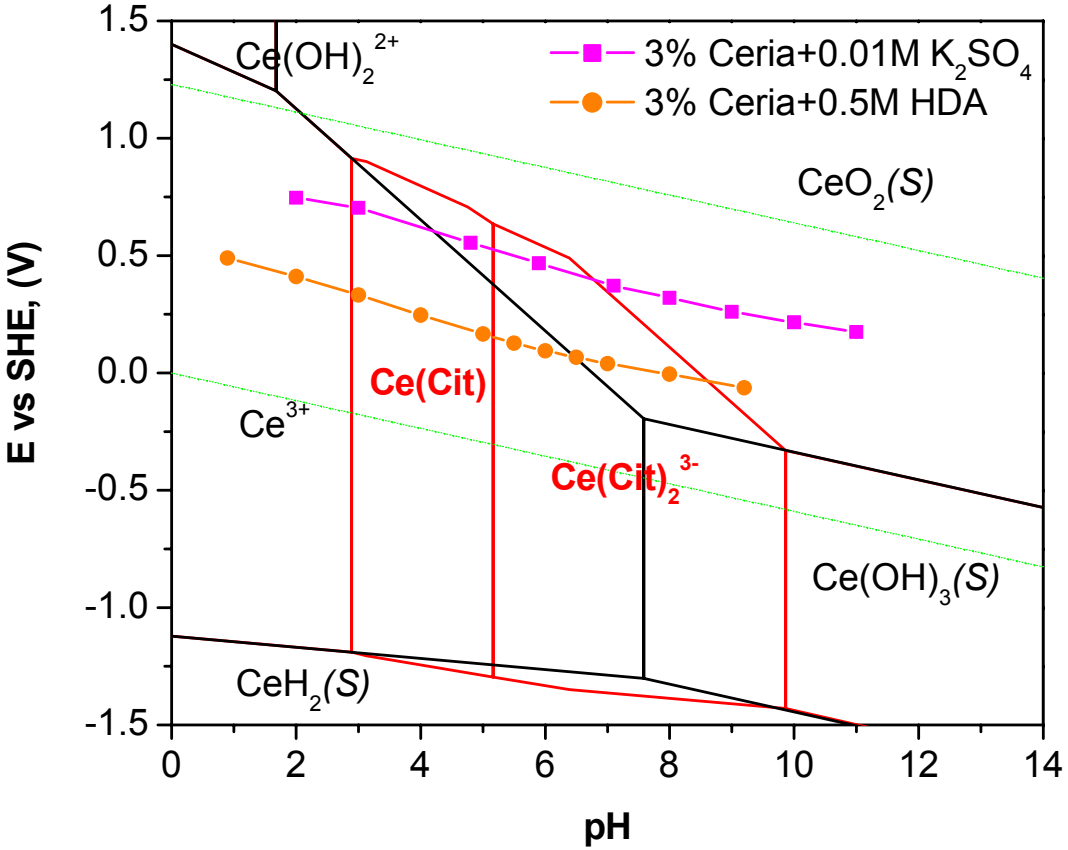


Potential-pH diagram of hydroxylamine-water system overlaid on Ce-water system

In a sulfate system, the Ce^{3+}/CeO_2 equilibrium intersects the solution redox at pH 3

Addition of hydroxylamine lowers the redox potential of the system - Ce^{3+}/CeO_2 equilibrium intersects the solution redox at pH 6

Potential-pH Diagram of Ce-Citric acid-H_2O System

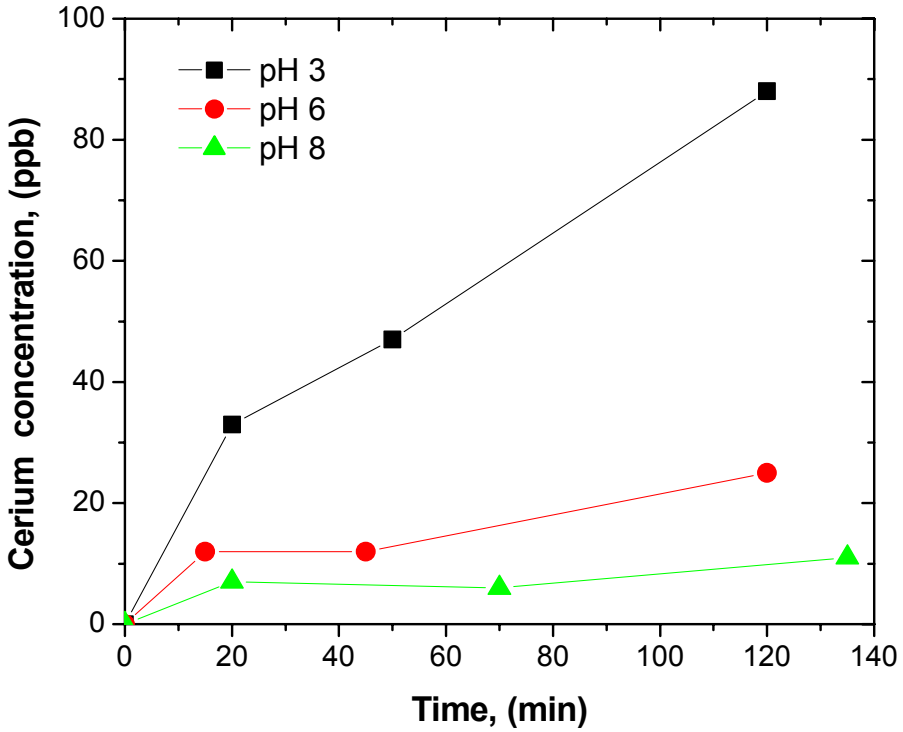


Potential-pH diagram of Ce-citric acid-water system overlaid on Ce-water system

Ce is complexed by citrate ions- Ce(Cit) and $Ce(Cit)_2^{2-}$

Due to the complexation, CeO_2 can be dissolved at higher pH conditions (pH 9)

Dissolution of Ceria in Hydroxylamine Solutions

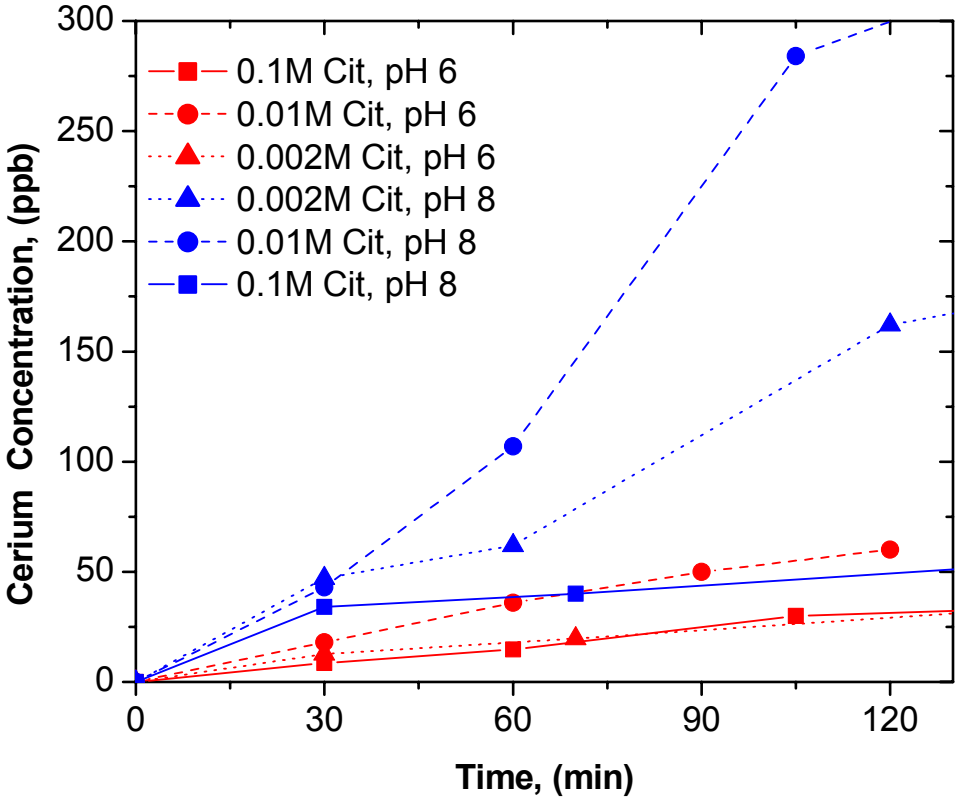


0.5M hydroxylamine solution

0.01% ceria

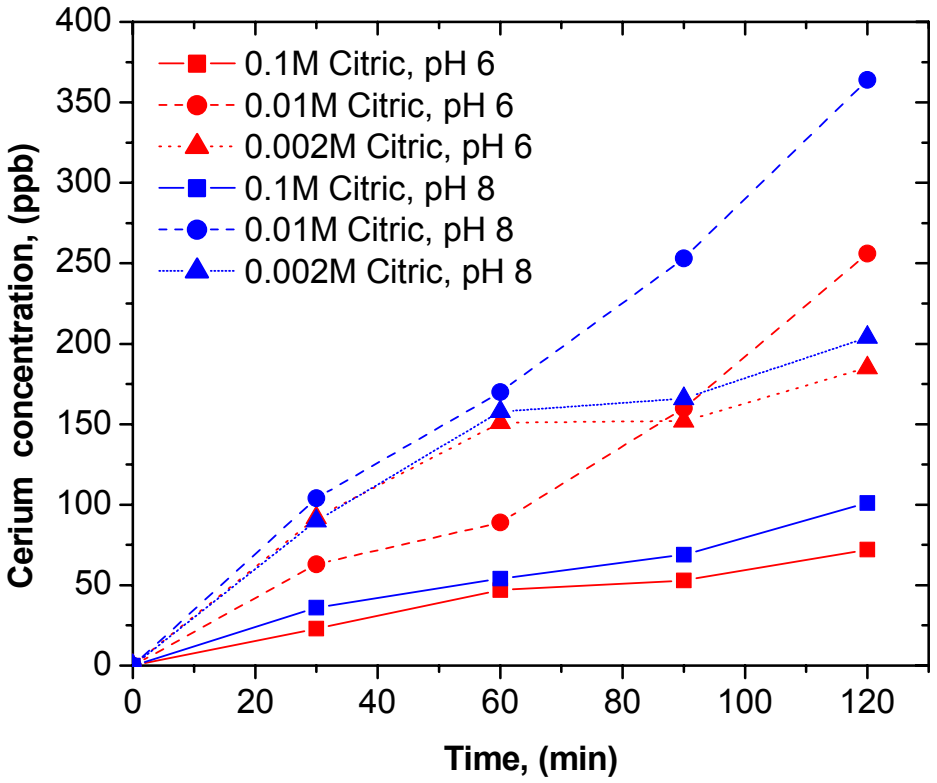
Kinetics of dissolution of ceria is pH dependent

Dissolution of Ceria in Hydroxylamine + Citric acid Solutions



- 0.5M hydroxylamine solution with varying levels of citric acid
- 0.01% ceria
- Dissolution at pH 8 > pH 6
- Highest dissolution at 0.01M citric acid (dissolution is suppressed at 0.1M citric acid)

Dissolution of Ceria in Citric acid Solutions



Solution with varying levels of citric acid (No hydroxylamine)

0.01% ceria

Dissolution at pH 8 ~ pH 6

Highest dissolution at 0.01M citric acid

Absence of hydroxylamine increases dissolution at pH 6

Proposed Redox Reactions

Oxidation:

$NH_2OH + NH_3OH^+ \rightarrow NO_2^- + NH_4^+ + 3H^+ + 2e^-$ $\quad E^o_{oxdn} = 0.162$ V

Reduction:

$CeO_2 + e^- + H^+ + H_2O \rightarrow Ce(OH)_3$ $\quad E^o_{redn} = 0.070$ V

Overall:

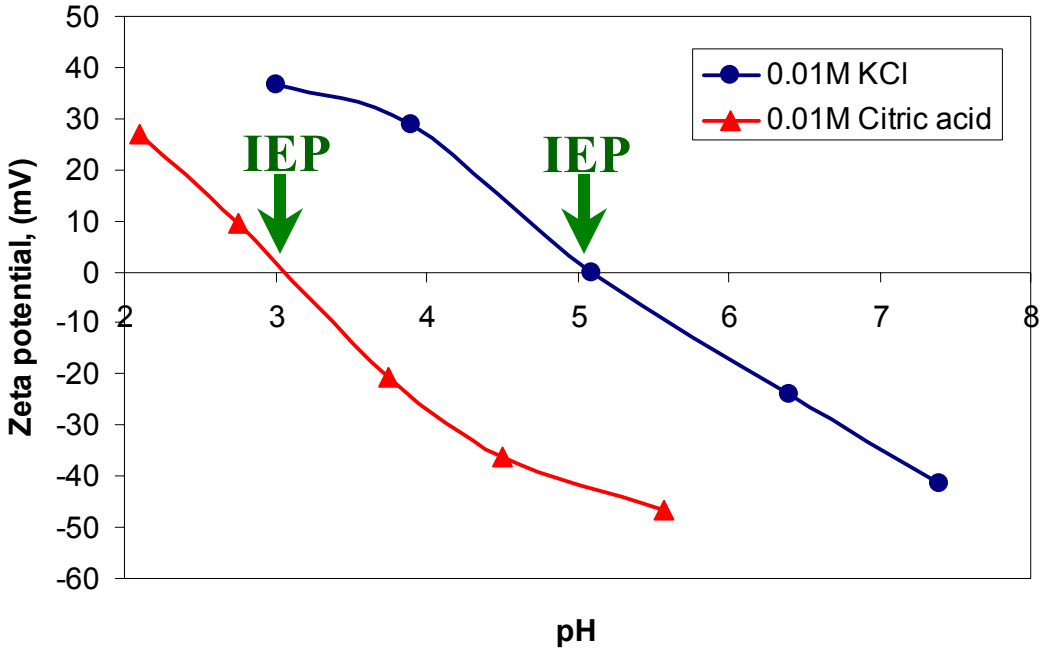
$2CeO_2 + NH_2OH + NH_3OH^+ + 2H_2O \rightarrow 2Ce(OH)_3 + NO_2^- + NH_4^+ + H^+$

$E^o = 0.232$ V

Formation of $Ce(OH)_3$ is possible due to the redox behavior of hydroxylamine

Formation of $Ce(OH)_3$ instead of Ce^{3+} lowers the dissolution rate of ceria in the presence of hydroxylamine

Zeta Potential - Ceria particles



Isoelectric point (IEP) of ceria in typical salt solution is at pH 5

Citric acid adsorbs on ceria particles – Shifts IEP to lower value- pH 3

Cleaning Tests

8” CVD oxide wafers

Polish process:

2psi/1psi/100rpm/107rpm/200ml/20sec

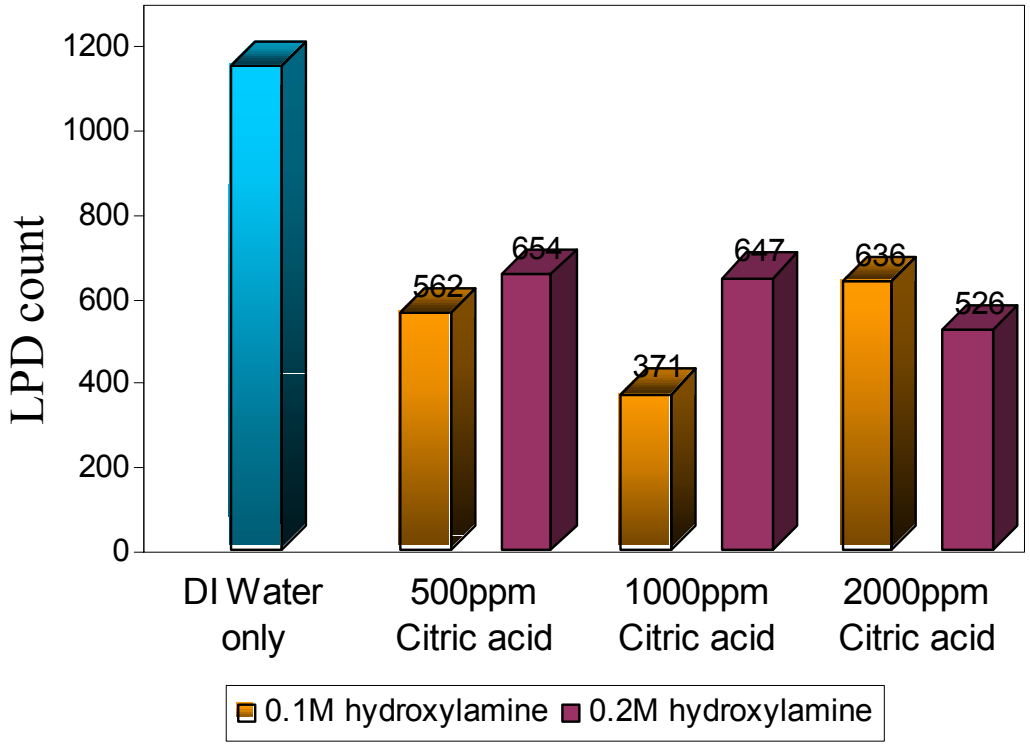
Buff process:

1psi/0.5psi/100rpm/107rpm/DIW/10sec

Megasonic cleaning – 10 cycles

Finally surface was scanned for particles with KLA SP1 @ 0.19µm

Effect of Citric acid Concentration on Cleaning



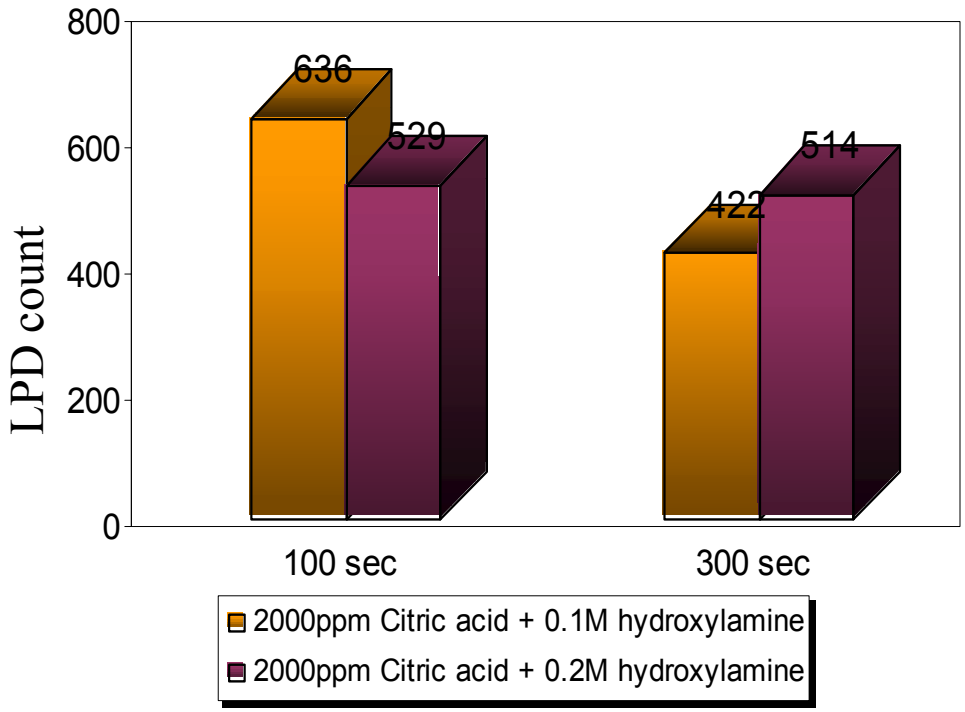
Solution pH = 8

Cleaning time = 100 Sec

Effective cleaning at lower levels of hydroxylamine

1000ppm citric acid (~0.05M) with 0.1M hydroxylamine has the best result

Effect of Cleaning Time



Solution pH = 8

# of particles decrease with cleaning time

Decrease is strongly visible in 0.1M hydroxylamine + 2000ppm citric acid system

Conclusions

Redox reactions between hydroxylamine and ceria do not increase the kinetics of ceria dissolution

Hydroxylamine could enable the formation of metastable $Ce(OH)_3$ around pH 6

Addition of citric acid enhances the dissolution rate

Solution of hydroxylamine and citric acid at pH 8 can be used to remove ceria particles

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Post CMP Cleaning after W CMP

Background Information for Tungsten

- **Dilute NH_4OH has been a favorite for PCMP for removing particles after tungsten and oxide CMP**

  High pH takes advantage of zeta potential effect

- **Other PCMP solutions have been designed around TMAH chemistries**

  NH_4OH/TMAH solutions have had some success

  Adding EDTA as a chelator can improve metal ion removal

- **Potential problems are incomplete metal ion removal (slurry formulations may include low concentrations of transition metals), etching of polysilicon surfaces, difficulties in removing certain inhibitor films.**

T. M. Pan, et al JECS 149(6) G336 (2002)

BCS product (pH 4.2) used for W PCMP Cleaning

- Used in a major US fab to clean wafers planarized with a hydrogen peroxide and silica slurry
- LPDs reduction by more than 50% compared to standard ammonium hydroxide cleaning processes
- Particular issue of Fe contamination: EKC cleaning solution was able to reduce the levels of residual Fe by a factor of more than 10 times, compared to the standard ammonium hydroxide cleaning processes
- Oxide buff previously used to lower metal contamination eliminated, increasing throughput and reducing COO
- No Ti liner loss or Tungsten plug coring

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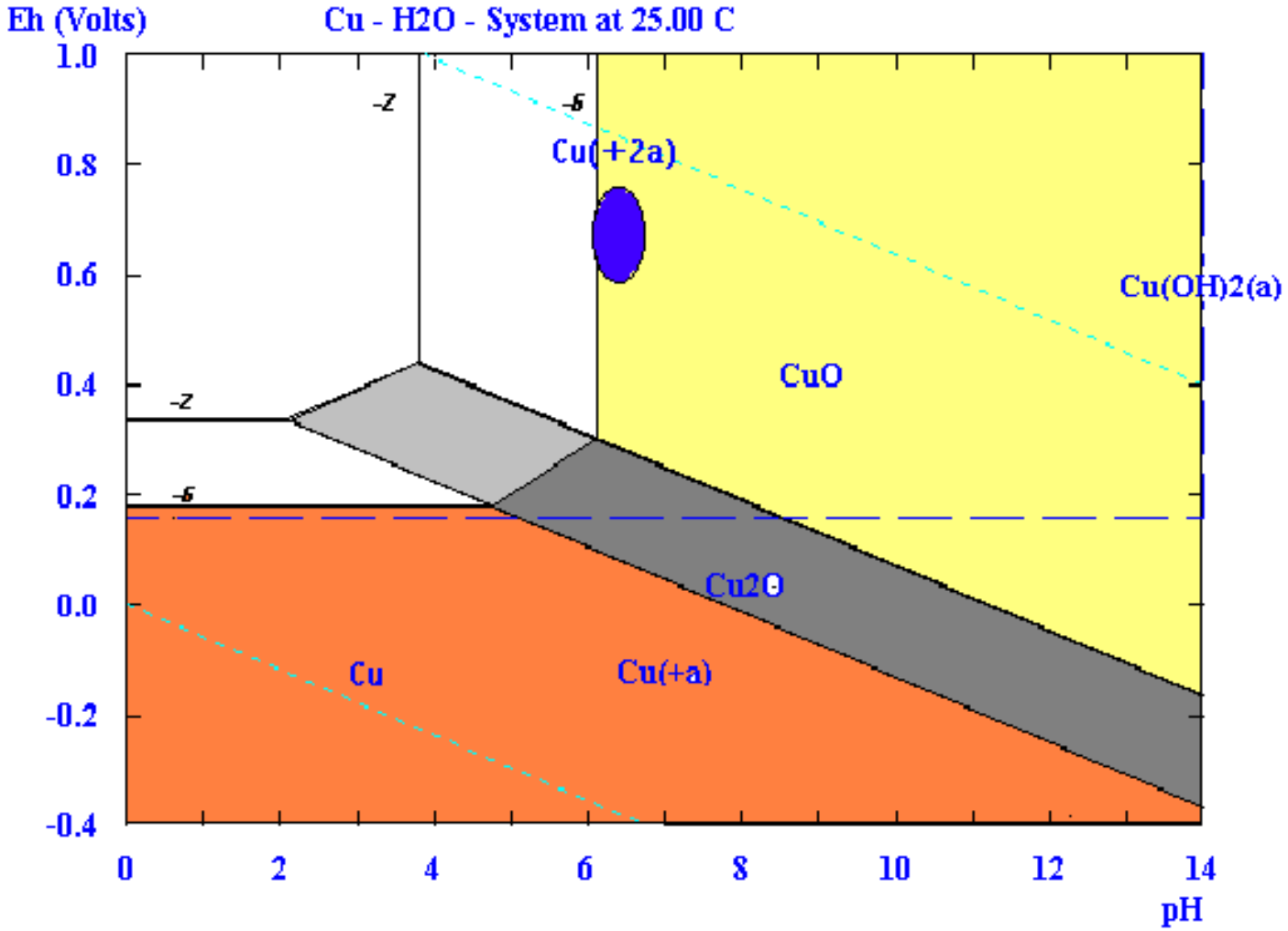
Post CMP Cleaning after Cu CMP

Desirable BCS Characteristics for Cu PCMP

- Aqueous, with pH ~ 7.5 (vs. pH 4.2)
- Contains additional chelating agents and anions
- Will not corrode sensitive metal films
- Can reduce brush loading from Cu oxides
- Wide process window
- Slurry waste drain compatible
- Environmentally safe
- Will not corrode CMP process equipment
- No sign of bacteria/fungus/mold/yeast growth
- No ammonium hydroxide
- No fluorides

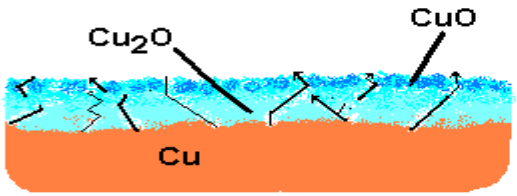
Copper Pourbaix



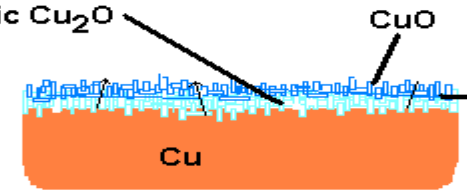
Copper Oxide Through the pH Ranges

pH 1 to 2

Hardness 1.7 GPa

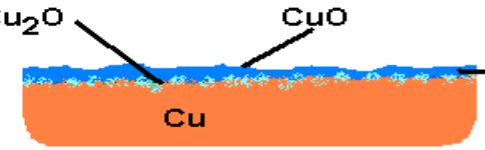


pH 3



Hardness ~4 GPa

pH 4 to 6



Hardness ~8 GPa

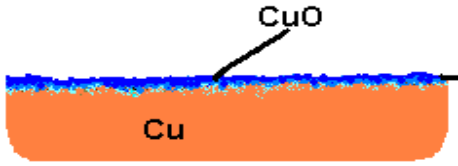
pH 7 to 9

Feng, Y. et. al.; Corrosion 53(5), p. 389-98 (1997)

Kobayashi, K., et. al.; Revue de Metallurdie 90(12) p. 1627-30 (1993)

Metikos-Hukovic, M. et. al.; J. Electrochem. Soc. 145(12) p. 4045-51 (1998)

Lee, S-H., MRS 2003, F2.9 CMP, p. 139 (San Francisco, CA April 21-25. 2003

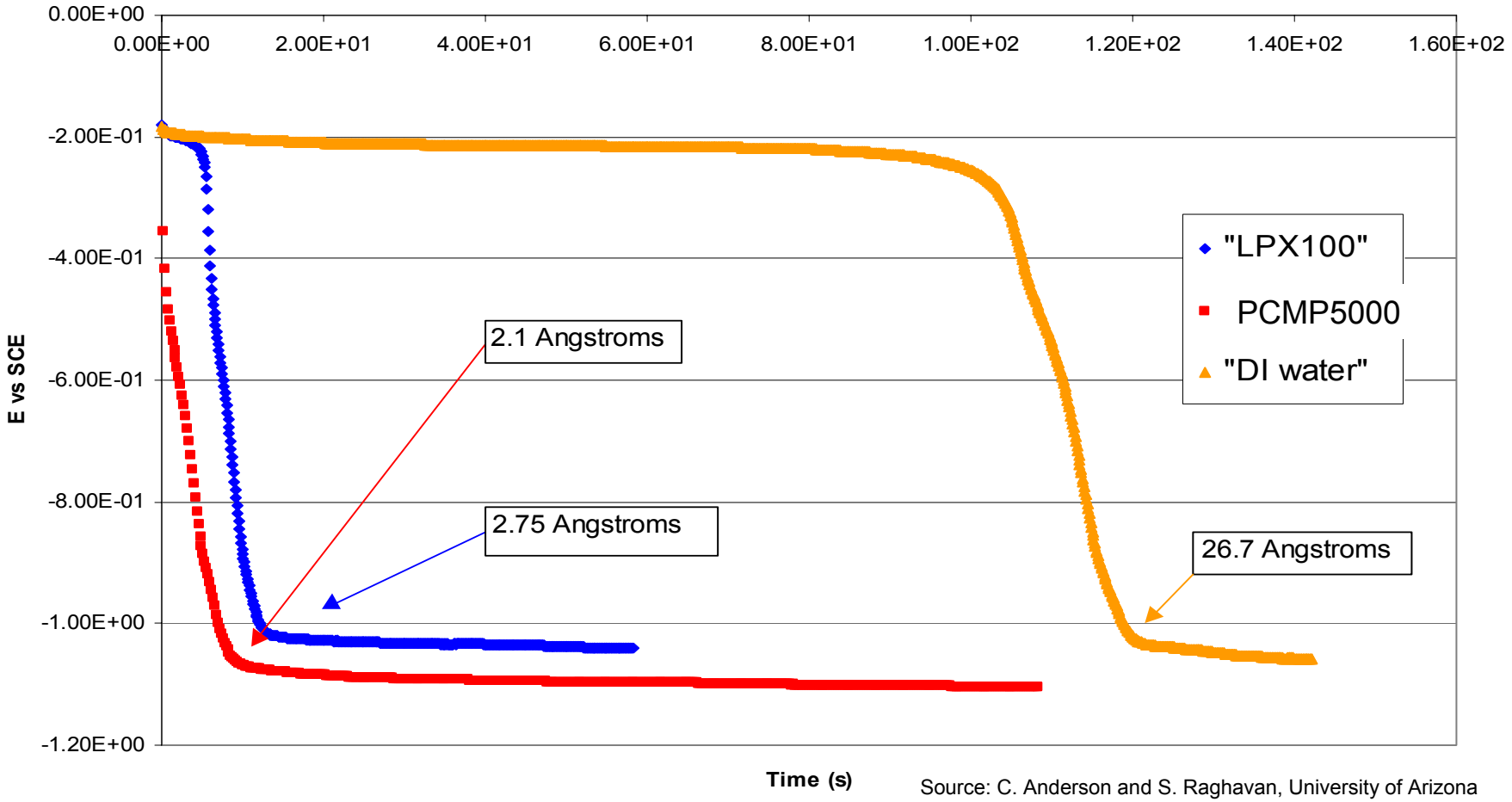


Hardness ~9

pH 10

Electrochemical Reduction of Copper Oxide

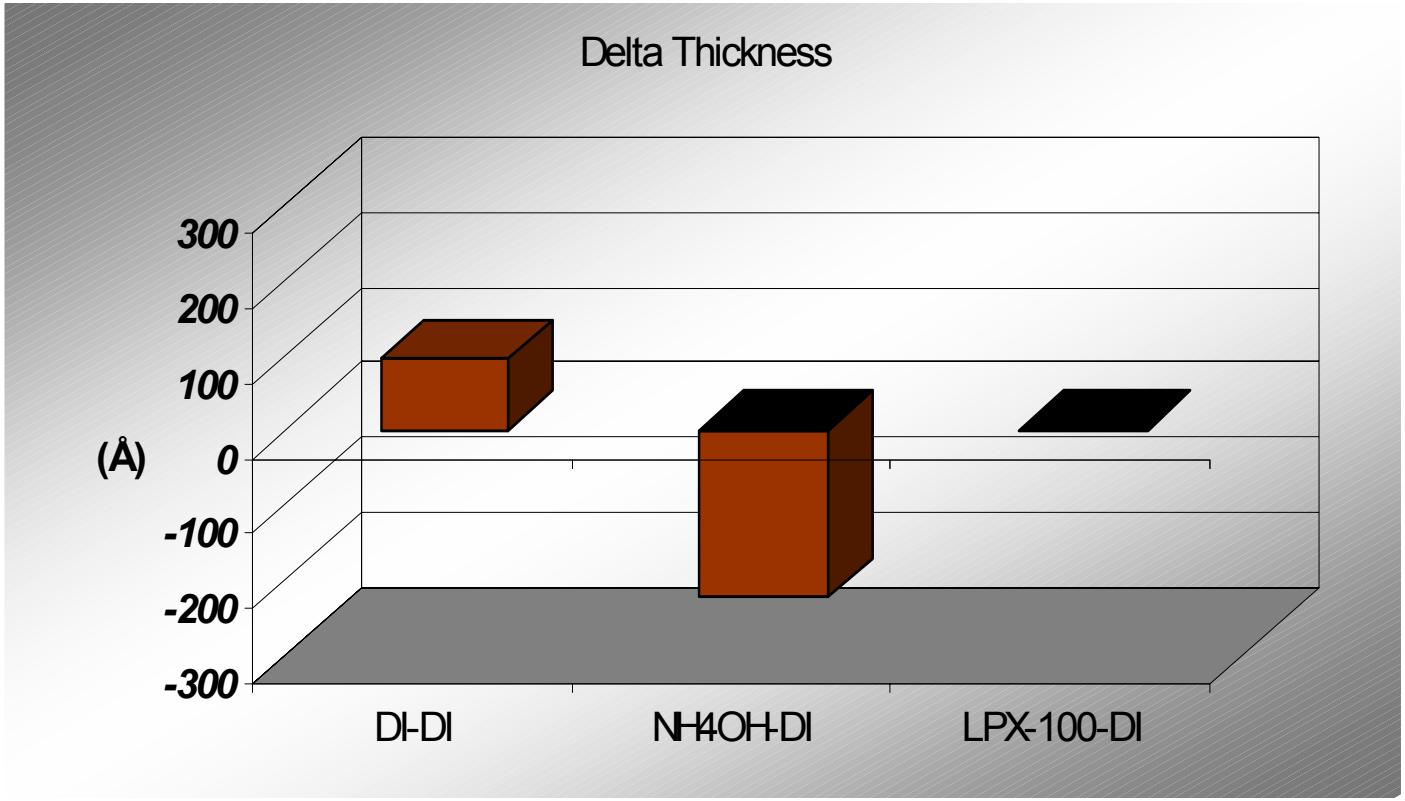
(Oxide thickness after 10 minutes of exposure of Cu to EKC solution)



Source: C. Anderson and S. Raghavan, University of Arizona

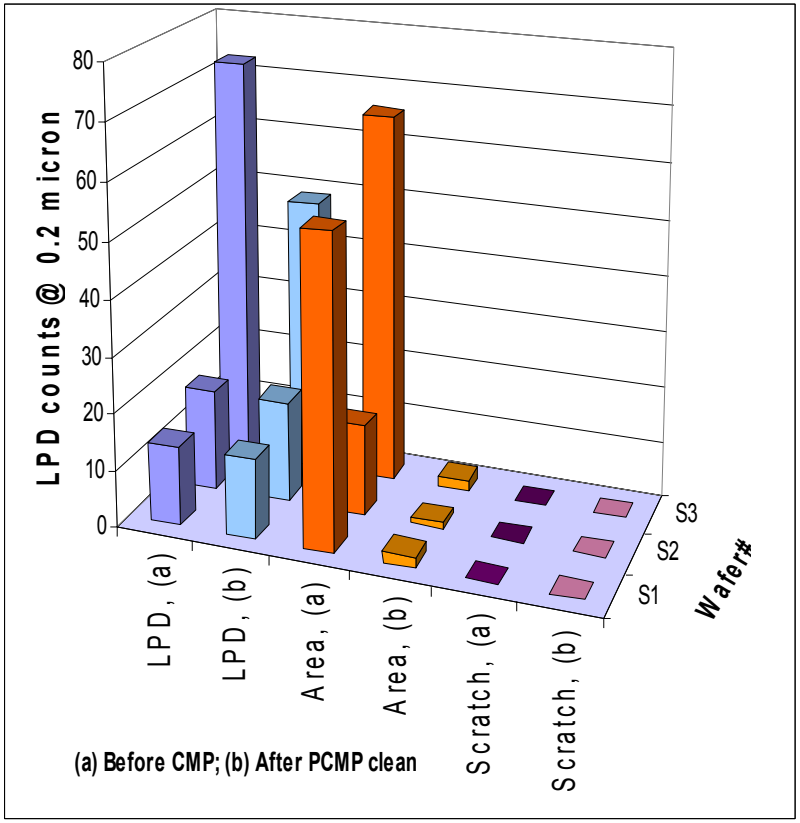
Comparison of Cu PCMP Cleaning Processes

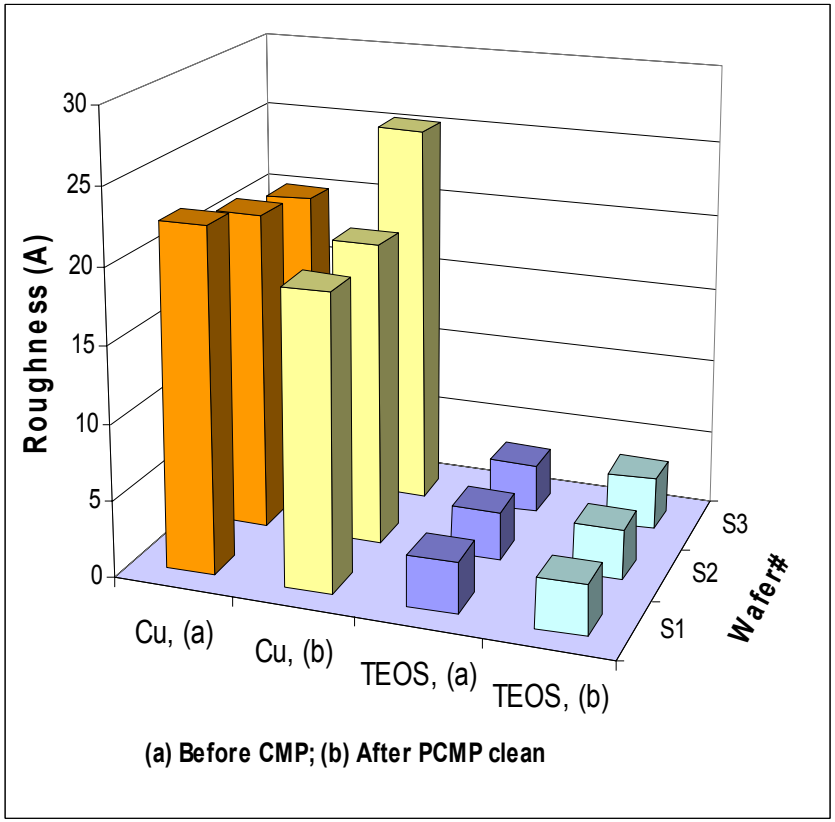
Copper thickness change (Dual-sided scrubber process)



Note: Negative number indicates thickness loss (corrosion)
Positive number indicates oxide growth on copper film
Dilution is 1:10 (LPX-100:DI Water)
Brush Box residence time is 10 seconds (2 brush boxes)

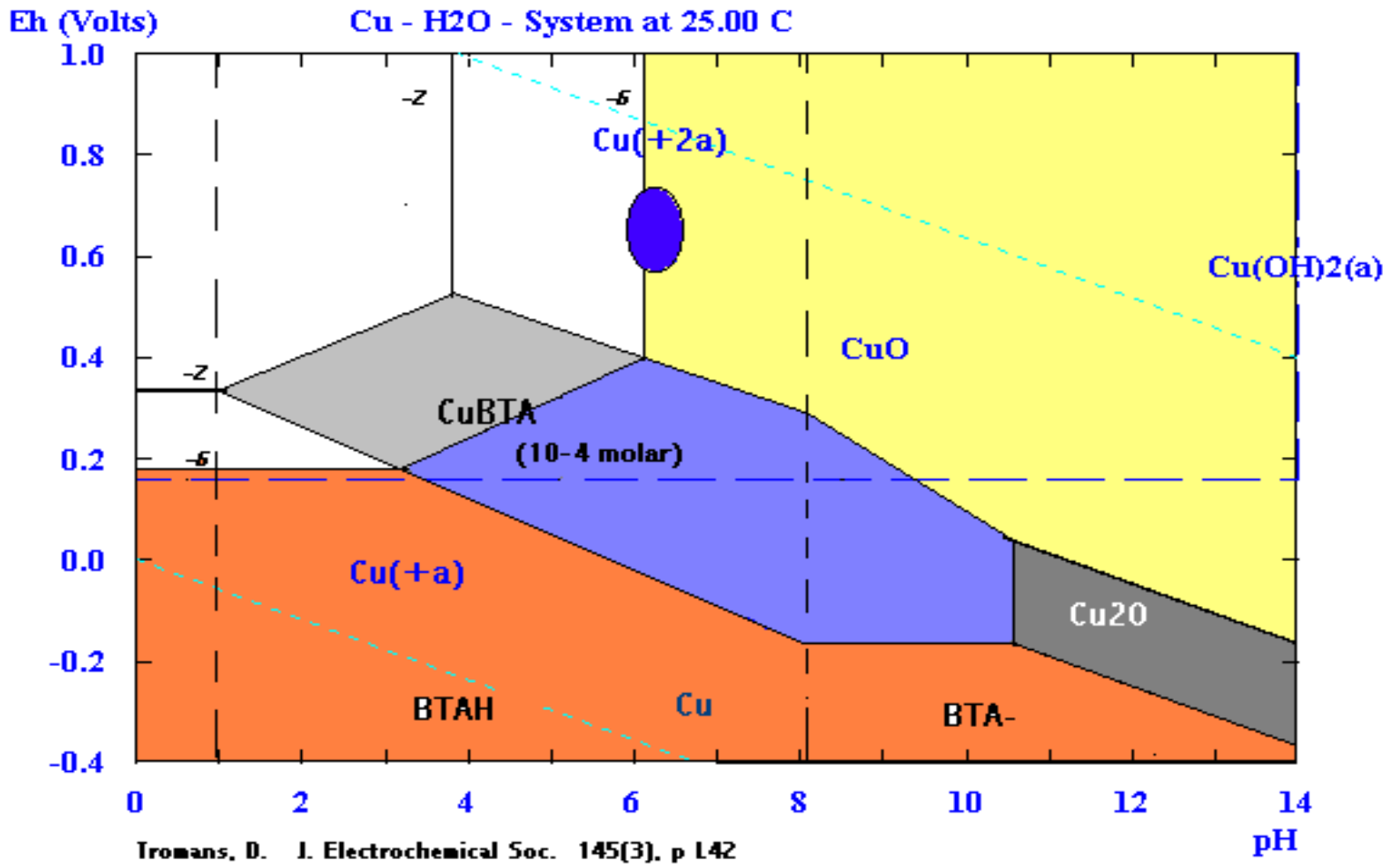
Defectivity and Surface Roughness on TEOS and Cu Wafers after Cleaning with BCS (pH 7.5)





TEOS and Cu wafers polished with EKC's Cu POR on 472 and cleaned

Pourbaix Diagram for Copper with BTAH



Electrochemical Evaluation of EKC PCMP Products for Removal of Benzotriazole (BTA) from Copper Surfaces

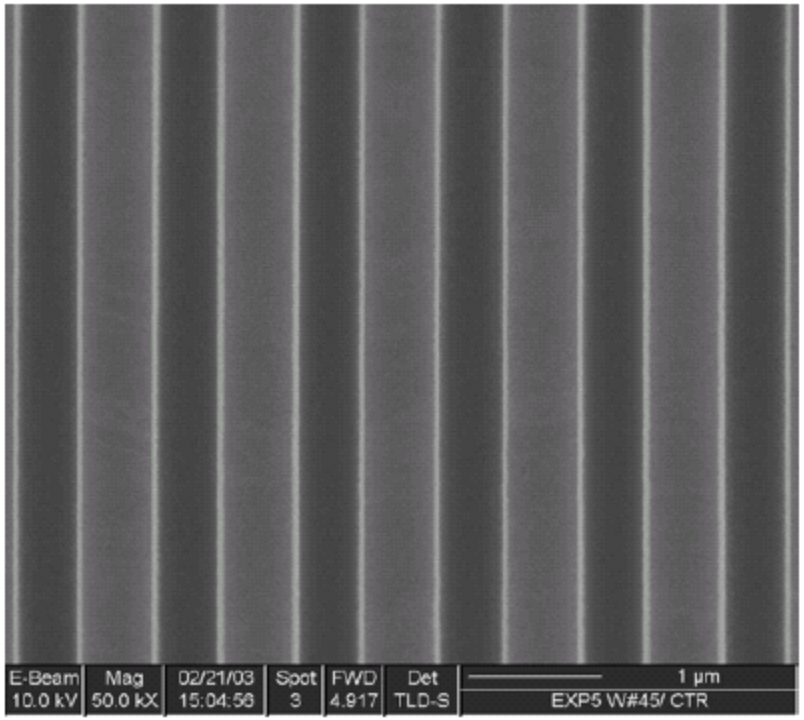
The results below demonstrate the removal of BTA from copper surfaces using LPX-100

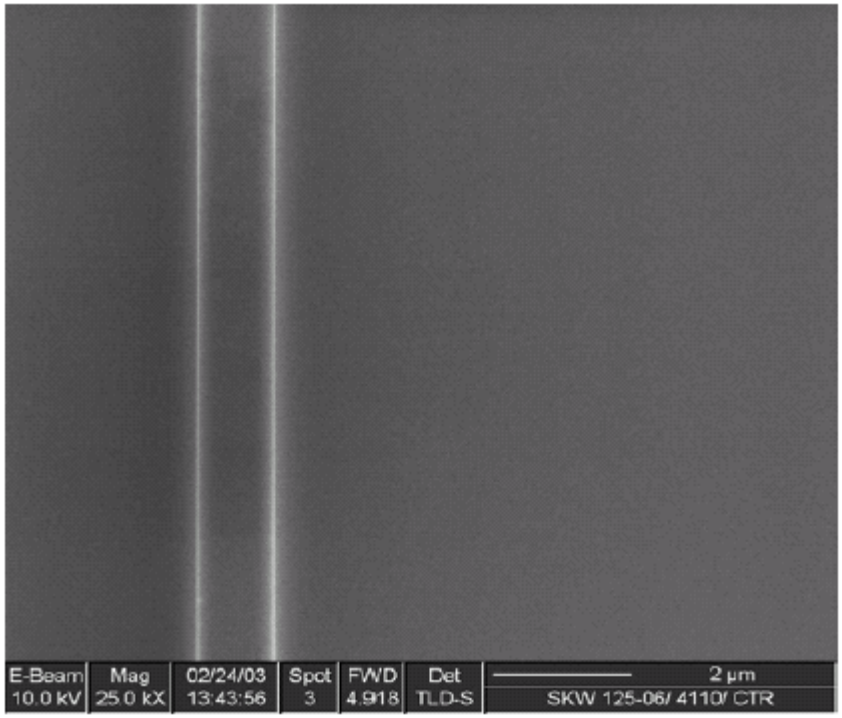
Copper coated silicon wafer pieces, 1cm x 3cm, were immersed in oxidizer solution containing 140 ppm benzotriazole (BTA) for ten minutes. This applied a protective layer of the BTA passivation agent to the surface of the copper pieces. A similar set of copper pieces were immersed in the same oxidizer solution without BTA for ten minutes. Both the BTA passivated and non-passivated pieces were tested electrochemically using a computer controlled Solartron Electrochemical Interface as operated by means of Scribner software.

Open Circuit Potential (OCP) measurements were conducted in fresh oxidizer solutions using the passivated and non-passivated pieces. Passivated pieces produced curves approaching +0.19V after a 500-second time frame. Non-passivated pieces produced curves approaching +0.075V. Fresh sets of both passivated and non-passivated pieces were rinsed in EKC LPX-100 for 3 minutes in glass beakers with stirring at 250 rpm. The piece rinsed with LPX-100 produced an OCP of +0.067V after 500 seconds

Post CMP Cleaning Results using pH 7.5 BCS with Optimized Megasonic + Brush + SRD

(Customer Data)





BCS (PCMP5510™) cleaned both Copper and Oxide

VPD-ICP/MS and TRXF Data for BD after Polishing

Black Diamond	VPD-ICPMS			TXRF
	Background	LPX-100	Polished/LPX-100	Polished/LPX-100
Ca	2.4	*	*	*
K	2.3	*	*	13 ± 54
Na	2.6	*	*	N/A
Al	48.0	5.3	58.0	N/A
Fe	2.9	0.2	1.6	1.1 ± 6.9
Cr	2.7	1.4	1.2	8.0 ± 12
Ni	0.3	0.3	0.4	5.4 ± 5
Zn	4.2	*	*	1.6 ± 4.0
Mg	0.5	0.5	*	N/A
Cu	0.6	2.8	1.0	*
S	N/A	N/A	N/A	180 ± 250
Cl	N/A	N/A	N/A	280 ± 140
Ti	N/A	N/A	N/A	*
V	N/A	N/A	N/A	7.3 ± 15
Mn	N/A	N/A	N/A	0 ± 9.6
Co	N/A	N/A	N/A	4.6 ± 5.5
Concentration=1E10 atoms/cm^2			* = at or below DL	

200mm Black Diamond blanket wafers were polished with EKC Barrier Slurry on IPEC 472. Wafers were cleaned in a DSS with 10% PCMP5510™.

BCS (PCMP5510™) Static Etch Rates and Stability

Film Type	Etch Rate (A/min)
Ta	0
TaN	0
Cu	< 1

- Tests run for 60 minutes at room temperature using full concentration (no dilution) to simulate worst-case scenario

- Typical manufacturing processes will be < 30 seconds cleaning time at 1:10 dilution (PCMP5510™:DI Water)

- pH range of 7.4 - 7.6 held over dilution range of 1:1 to 1:50

- No sign of bacteria/fungus/mold/yeast growth over several dilutions for up to 16 days. DI water showed high counts at 8 and 16 day intervals.

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Conclusion