Effect of CMP on abrasives and their surface characteristics

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Outline

- Introduction
- Common CMP slurry abrasives and additives
- Effect of additives and polishing on abrasives
- Some aspects of III-V polishing
- Contribution of pad to slurry waste
- Summary and Conclusions
- Acknowledgements

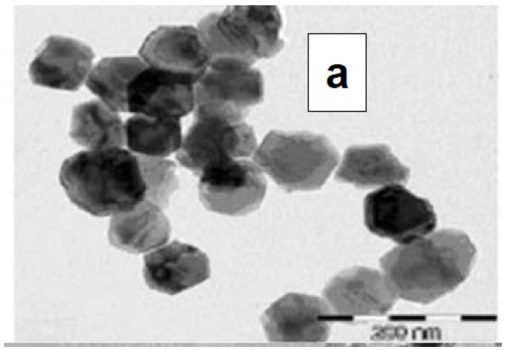
Common slurry components: BEOL

Substrate	Slurry Components	Species present post- polish
• Cu • Cu/Ta/TaN • Cu/Ti/Co • Cu/Ti/Ru • Cu/Mn • W • SiCOH	• Silica/Alumina • pH adjusting agents such as HNO_3, KOH, NH_4OH, etc. and buffers • Oxidizer (H_2O_2, Ferric nitrate, KIO_4, $KMnO_4$ etc.) • Complexing agents (amino acids such as glycine, carboxylic acids such as citric acid) • Corrosion inhibitors (BTA and its derivatives) • Surfactants	• OH-, surfactants/ adsorbed metal ions/ metal oxides and pad debris • dissolved, suspended and settled fine particles and dissolved metals • Unreacted oxidizers, complexing agents, inorganic ions, etc.

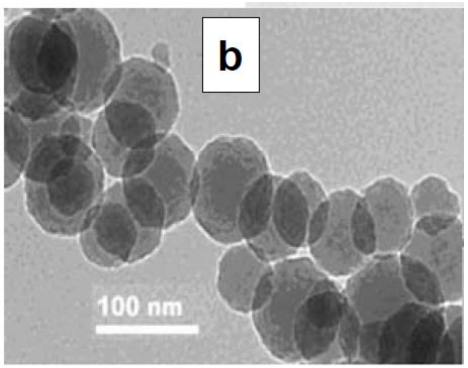
Common slurry components: FEOL

Substrate	Slurry Components	Species present post- polish
• SiO_2/Si_3N_4 • Poly-Si • W, Al • Ge • GaAs • InP • InGaAs • InAlAs	• Silica, Ceria • pH adjusting agents such as HNO_3, KOH, NH_4OH, etc. and buffers • Oxidizer (H_2O_2, etc.) • Surface modifying agents	• Arsenic rich waste • Dissolved AsH_3, PH_3 and NH_3 • Adsorbed metal ions • Unreacted Oxidizing agents • Inorganic ions • Unreacted complexing agents

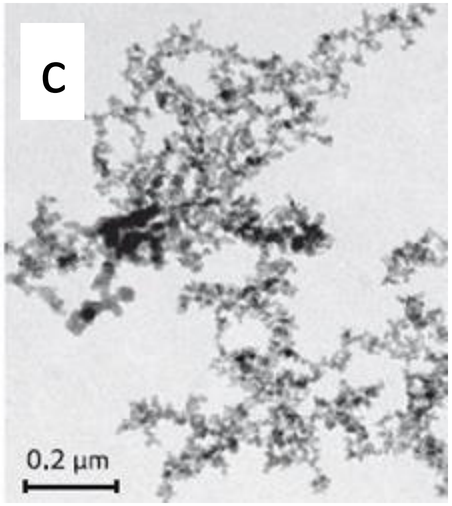
Common abrasives used in CMP and their characteristics



(a) Rhodia Ceria (d_m -60nm)



(b) Nexsil colloidal Silica (d_m-50 nm)

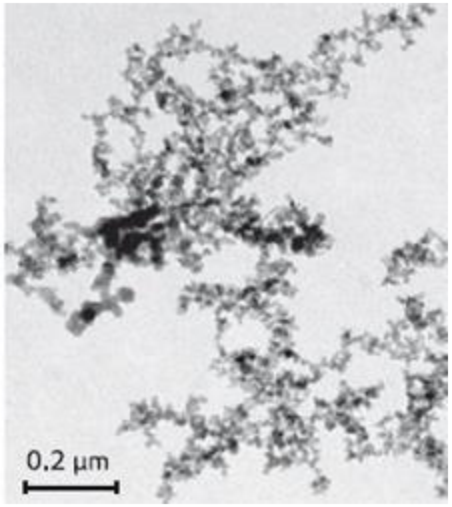


(c) Aerosil Fumed Silica (d_m- 130 nm)

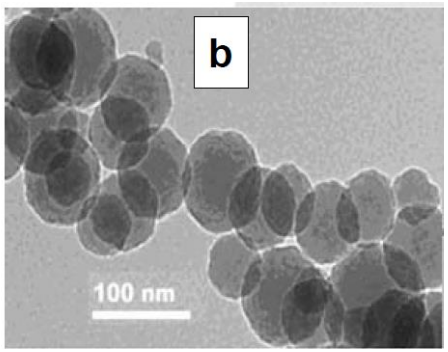
	Bulk density (g/cm^3)	Mohs Hardness	IEP	Possible species on surface
Silica	2.65	6-7	~2	$M-OH_2^+ \longrightarrow M-OH + H^+$ $M-OH \longrightarrow M-O^- + H^+$ **M= Metal**
Ceria	7.65	6	6-8	
Alumina	3.95	9.0	9	

- *H. Bergna et al., Colloidal Silica Fundamentals and Applications, Taylor and Francis, 2006*
- George V. Franks, and Yang Gan J. Am. Ceram. Soc., 90 [11] 3373–3388 (2007).

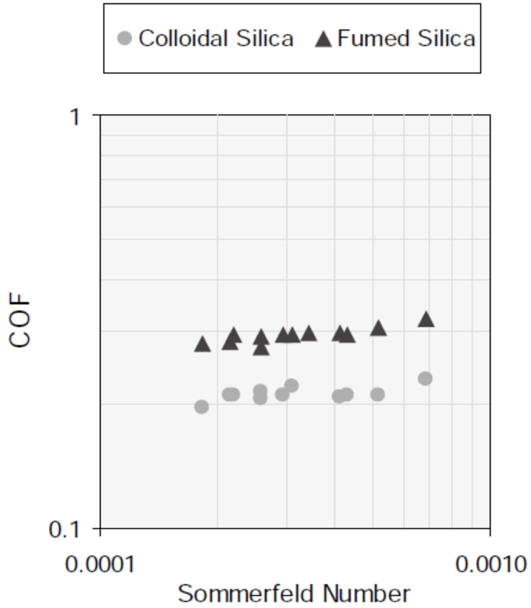
Differences between colloidal and fumed Silica



Aerosil Fumed silica



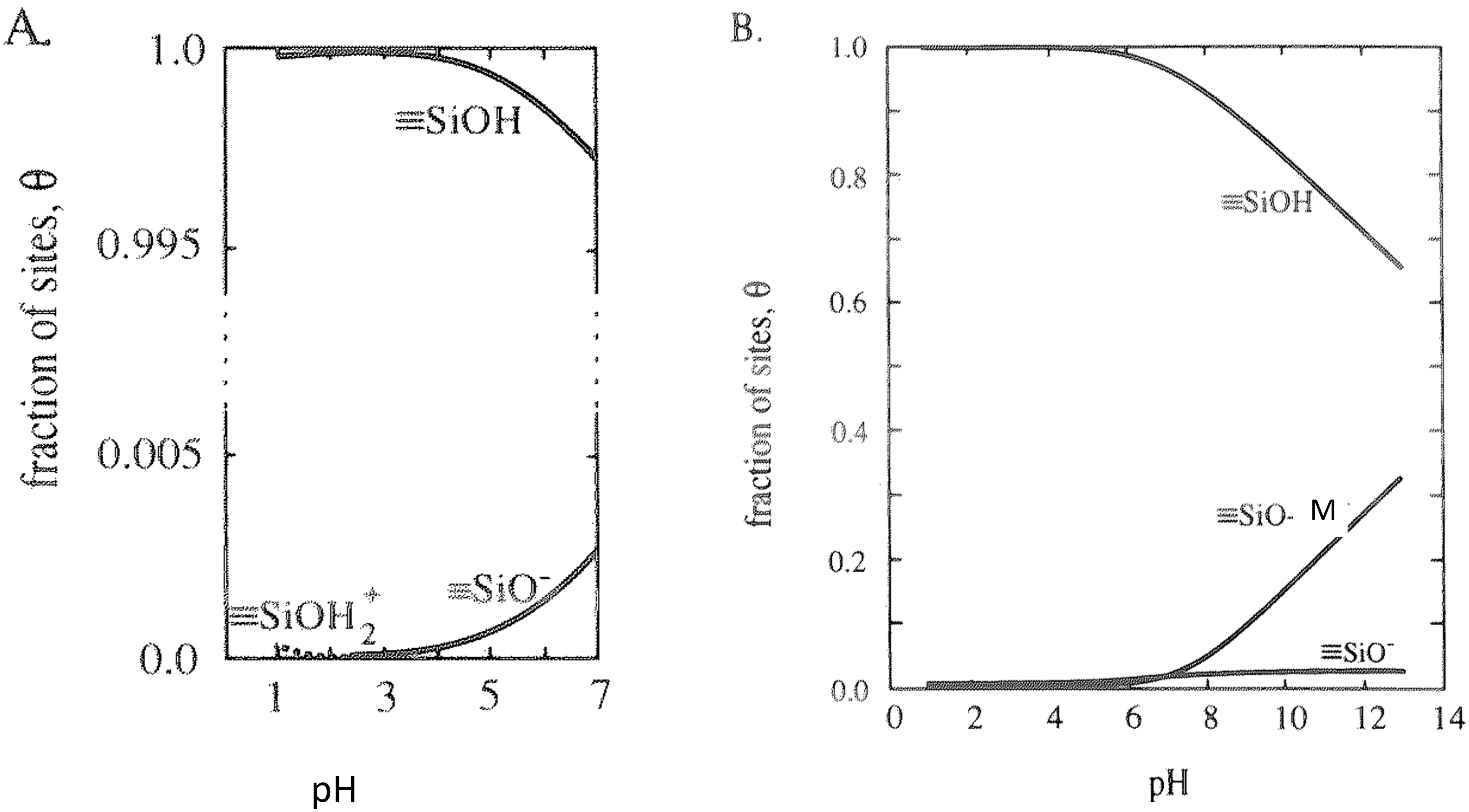
Nexsil 85A Colloidal silica



Fumed Silica	Colloidal Silica
Possible **Cl** contamination due to manufacture from chloro-silane (<200 ppm)	Possible **Na** contamination due the to manufacture from sodium silicate
Large hard and soft aggregates Generally used at high pH -> High Concentration of dissolved silica	Surfactants to maintain colloidal stability

- http://www.aerosil.com/product/aerosil/en/industries/papers/pages/default.aspx
- Z. Li, K. Ina, P. Lefevre, I. Koshiyama, and A. Philipossian. Journal of The Electrochemical Society, 152(4)G299-G304~2005.

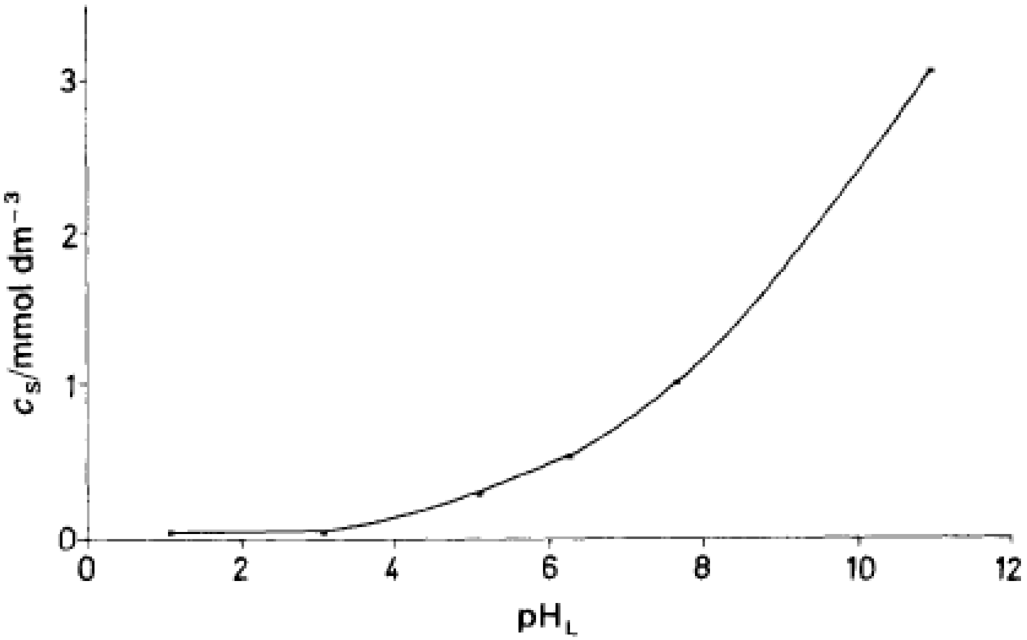
Silica Speciation



M= Cation from the pH adjusting agent (K^+, NH_4^+)

- Dove and Elston. Geochimica et Cosmochimica Acta. Volume 56, Issue 12. December 1992, Pages 4147–4156.

Solubility of Silica as a f(pH)



Saturation concentration of silica, (C_s) as a function of pH

Silica can dissolve as a silicate as shown below:

$$-SiO_2 + 2OH^- \longrightarrow Si(OH)_2O_2^{-2}$$

Can form insoluble species quickly when they react with metal cations (Ca^{+2}, Zn^{+2} and other heavy metal impurities)

- Wolfram Vogelsberger,* Andreas Seidel and Georg Rudakoff. CHEM. SOC. FARADAY TRANS., 1992, 88(3), 473-476

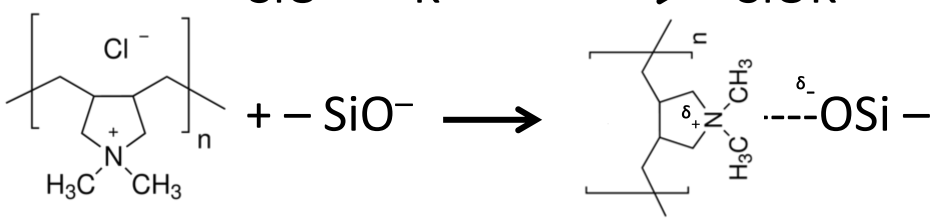
Possible interactions and metal impurities on silica surface

Electrostatic Interactions :

Adsorption of cationic surfactants/stabilizers and metal ions.

$$-SiO^- + C_{19}H_{42}N^+ \text{ (CTAB)} \longrightarrow -SiO\ C_{19}H_{42}N$$

$$-SiO^- + K^+ \longrightarrow -SiOK$$



Acid-Base Reactions:

$$-SiOH + NH_4OH \longrightarrow -SiO\ NH_4 + H_2O$$

	Metal	Conc. (ppb)
1	Al	50
2	Ca	110
3	Cr	22
4	Cu	10
5	Fe	85
6	Mg	20
7	Ni	11
8	K	50
9	Na	20
10	Zn	11

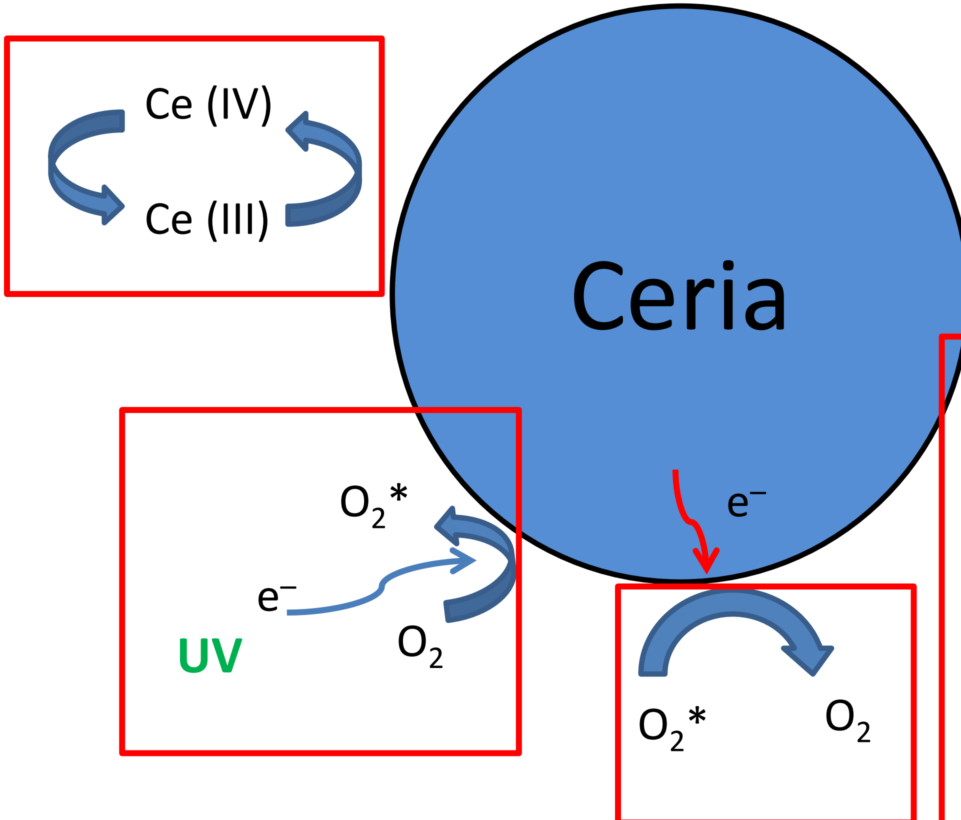
Trace Metal Contamination in fumed silica slurries measured with ICP-AES

- *Yamada et al.,* Journal of The Electrochemical Society, 158 (8) H830-H835 (2011)

Possible interactions on ceria surface

Acid-Base Reactions:

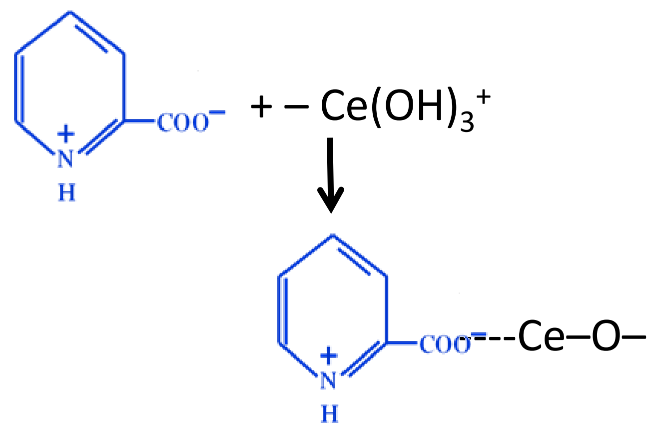
$$2CeO_2 + NH_2OH + NH_3OH^+ + 2H_2O \longrightarrow 2Ce(OH)_3 + NO_2^- + NH_4^+ + H^+$$



Excellent catalyst for many reactions

Electrostatic:

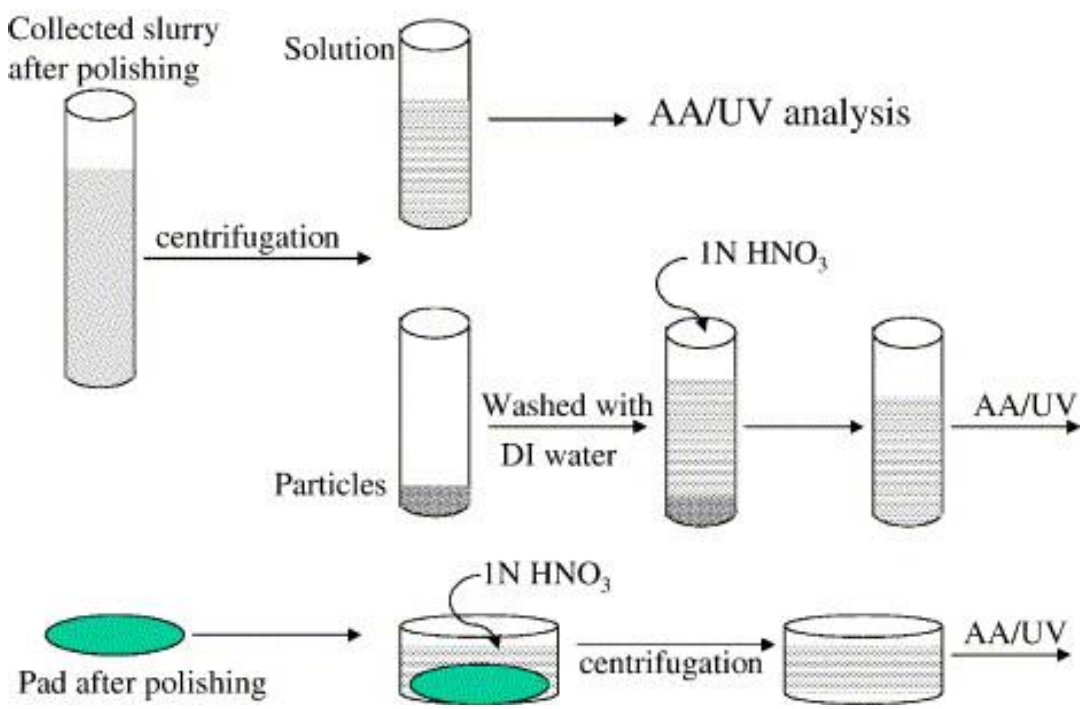
$$Si\text{-}O^- + Ce(OH)_3^+ \longrightarrow Si\text{-}O\text{-}Ce(OH)_3$$

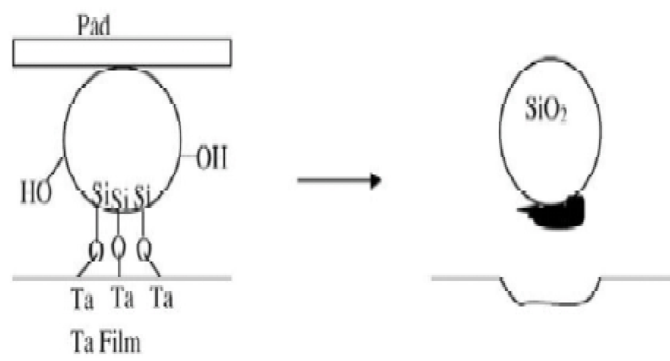


Switchable oxidation states: ROS generation/ ROS consumption

Effects of polishing on the abrasives

Cu/Ta barrier CMP - Where does the polished metal go?





Using silica to polish Ta (Ta_2O_5)

- *Ying Li, Junzi Zhao, Ping Wu, Yong Lin, S.V. Babu, Yuzhuo Li. Thin Solid Films, Volume 497, Issues 1–2, 21 February 2006, Pages 321–328.*
- Y Li, M Hariharaputhiran, S.V Babu J. Mater. Res., 16 (2001), p. 1066
- *A. Vijayakumar, T. Du, K.B. Sundaram, V. Desai, Polishing mechanism of tantalum films by SiO_2 particles, Microelectronic Engineering 70 (2003) 93-101*

Ta CMP results using modified and unmodified silica in water

Location found	*Fumed Silica*		*Modified silica*	
	Ta detected (mg)	% Ta detected	Ta detected (mg)	% Ta detected
Solution	0.33	22	< 0.2	100
Abrasive	1.13	**75.3**	ND	ND
Pad	0.04	2.7	ND	ND
Total detected	1.5	100	< 0.2	100
Ta loss from disk per polish	1.63		< 0.2	
MRR (nm/min)	73.4		< 9	

Colloidal silica also shows a similar behavior

- *Ying Li, Junzi Zhao, Ping Wu, Yong Lin, S.V. Babu, Yuzhuo Li. Thin Solid Films, Volume 497, Issues 1–2, 21 February 2006, Pages 321–328*

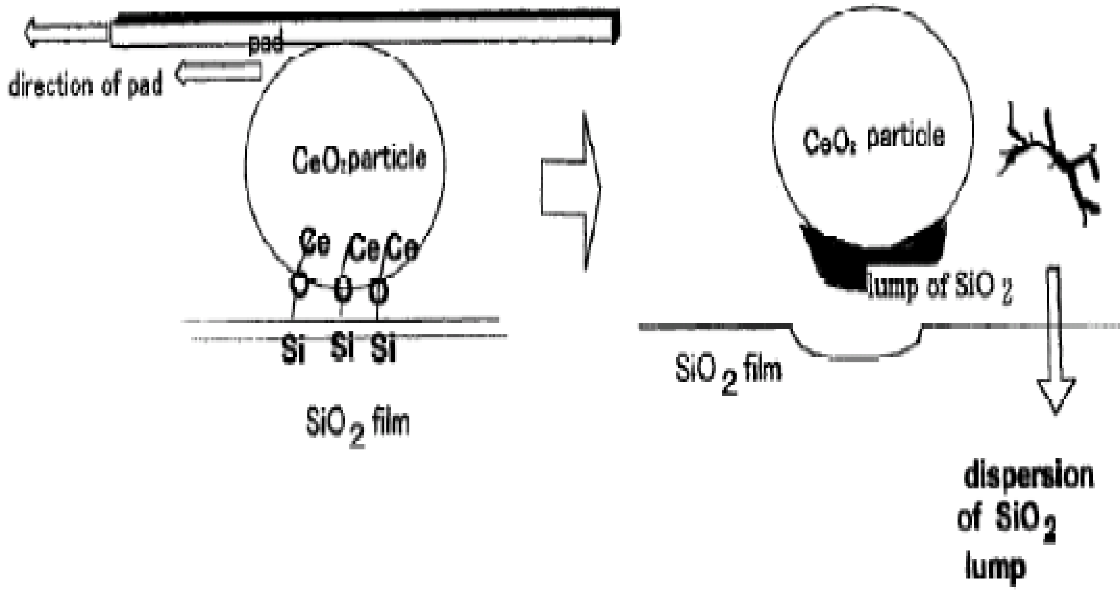
Cu CMP results using silica or alumina with 1% glycine and 1% H_2O_2

Location found	Fumed Silica		Alumina	
	Cu detected (mg)	% Cu detected	Cu detected (mg)	% Cu detected
Solution	2.2	**47.8**	16.6	**88.3**
Abrasive	2	**43.5**	1.5	8
Pad	0.4	8.7	0.7	3.7
Total	4.6	100	18.8	100
Cu loss from disk per polish	5.1		20.8	
MRR (nm/min)	429		1750	

Colloidal silica also shows a similar behavior

Ref: *Ying Li, Junzi Zhao, Ping Wu, Yong Lin, S.V. Babu, Yuzhuo Li. Thin Solid Films, Volume 497, Issues 1–2, 21 February 2006, Pages 321–328*

Polishing Mechanisms of SiO_2 with Ceria

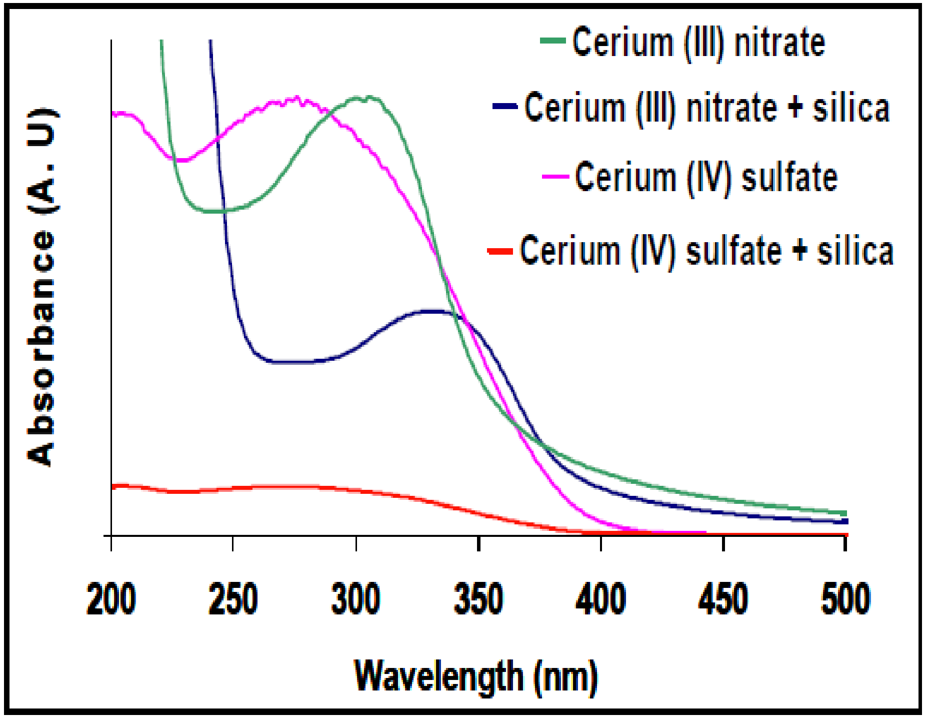


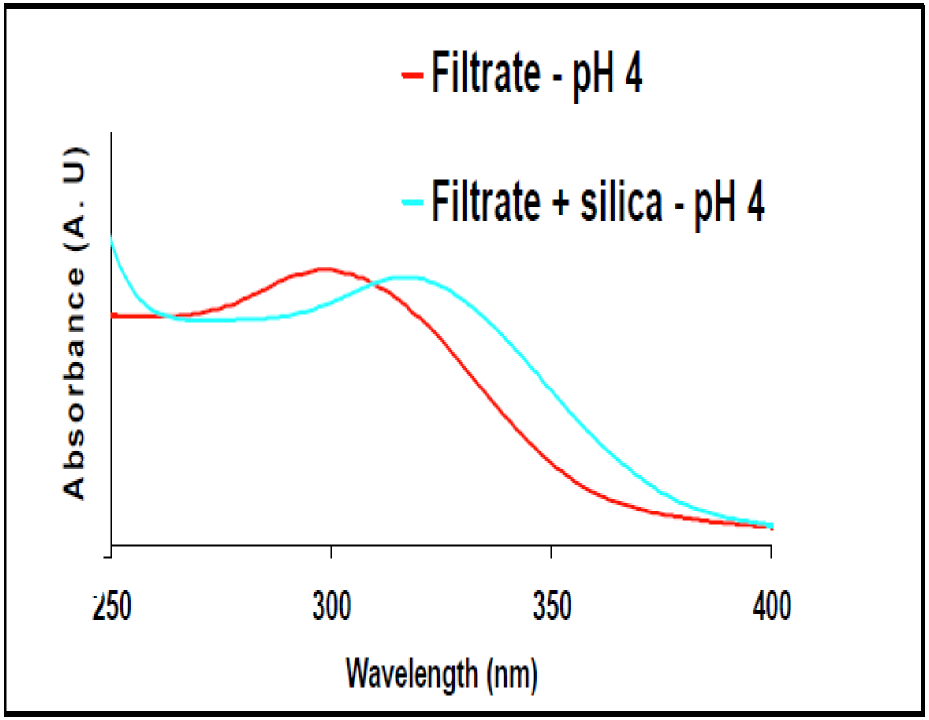
Using Ceria to Polish SiO_2

Polishing mechanisms give an idea of the possible species on the surface of nanoparticles in the slurry waste.

- *Lee Cook,* Journal of Non-Crystalline Solids 120 (1990) 152-171
- *Tetsuya Hoshino, Yasushi Kurata, Yuuki Terasaki, Kenzo Susa, Mechanism of polishing of SiO_2 films by CeO_2 particles. Journal of Non-Crystalline Solids 283 (2001) 129-136*

UV-Vis Absorbance (Reactivity of Ce^{3+} salt)

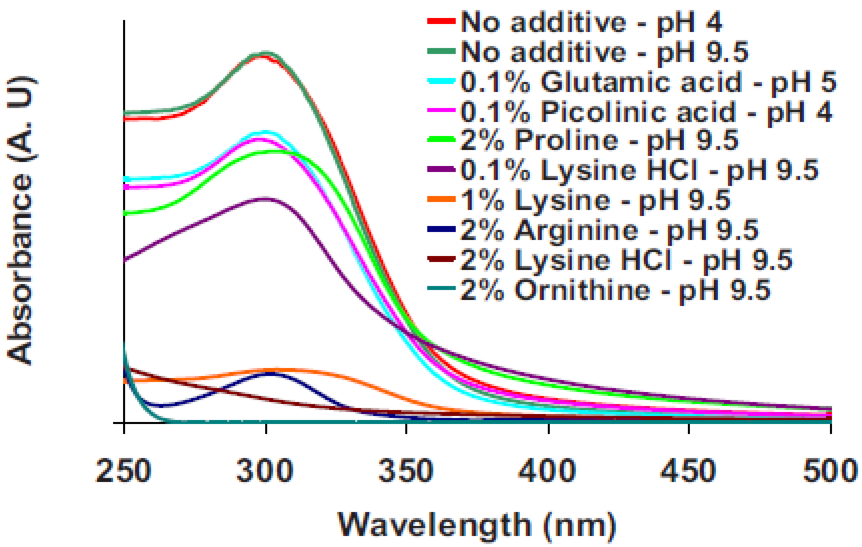


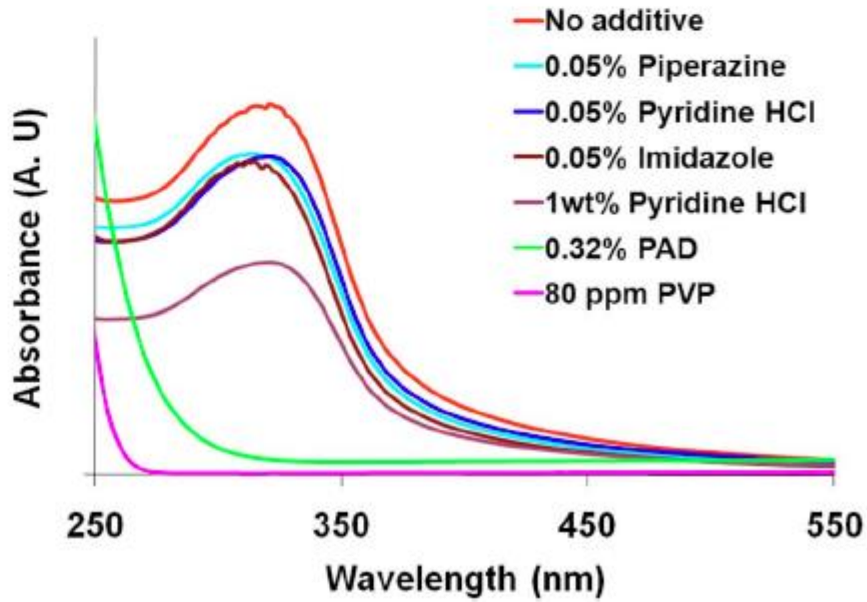


This shift in the peak corresponds to **Ce-O-Si** structures

Ref: *Veera Dandu, PhD. thesis. Clarkson University*

Interaction of ceria with different additives

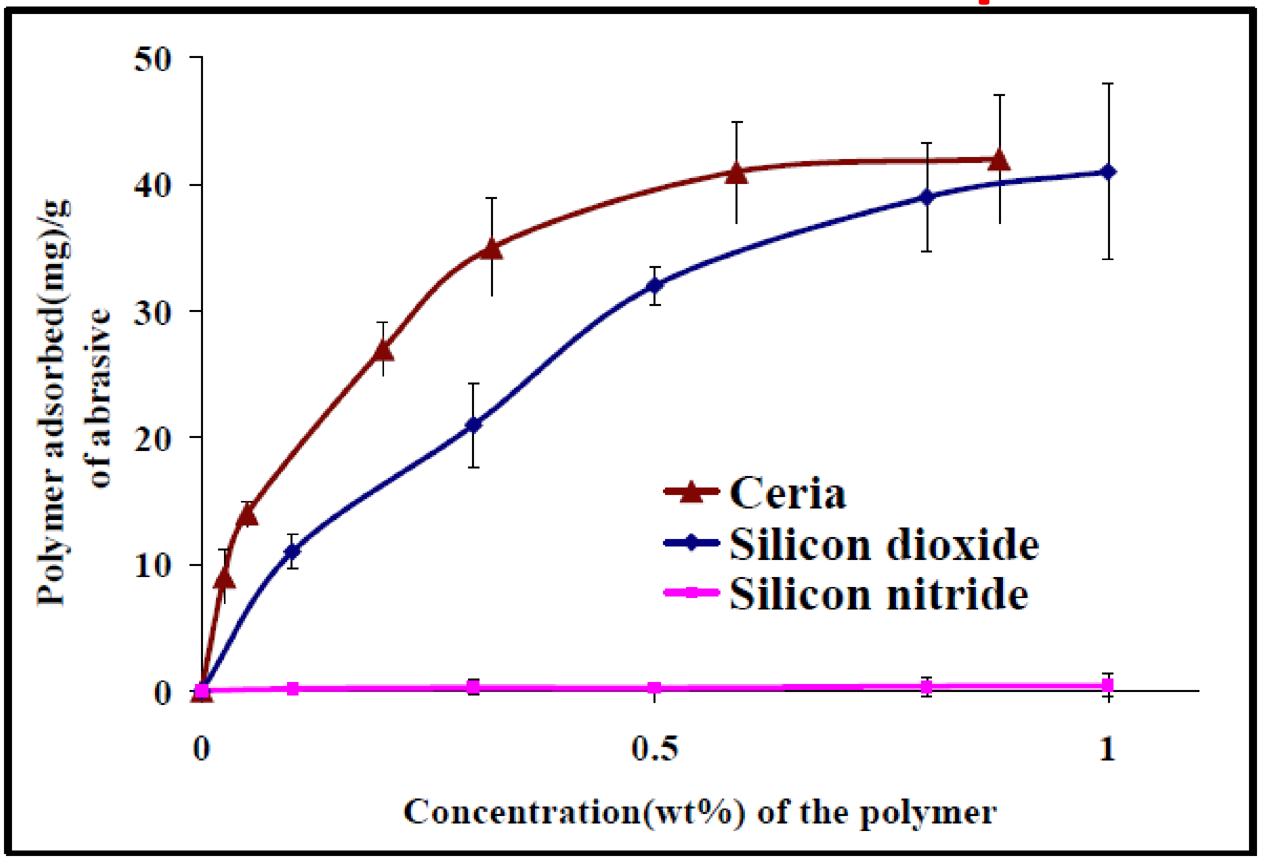


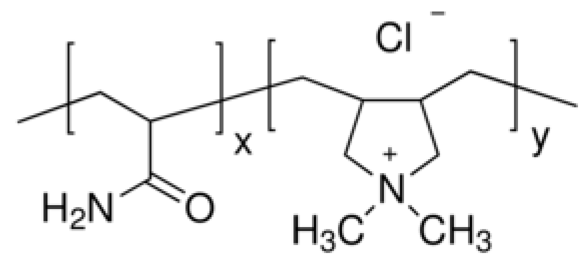


- The RRs of Oxide with the slurries having lower peaks were low (<2 nm/min).
- The absence of the absorbance peak is due to the blocking of all the Ce^{+3} species on the surface of the ceria particles

Ref: *Veera Dandu, PhD. thesis. Clarkson University*

Adsorption Isotherms showing the adsorption of "PAD" on different particles at pH 4





Poly (acrylicacid-co-diallyl-dimethyl ammonium chloride) (PAD)

Dispersions : 0.25wt% ceria (d_m ~60 nm), 10wt% silicon dioxide (d_m ~ 50 nm) and 10wt% silicon nitride (d_m ~ 50 nm)

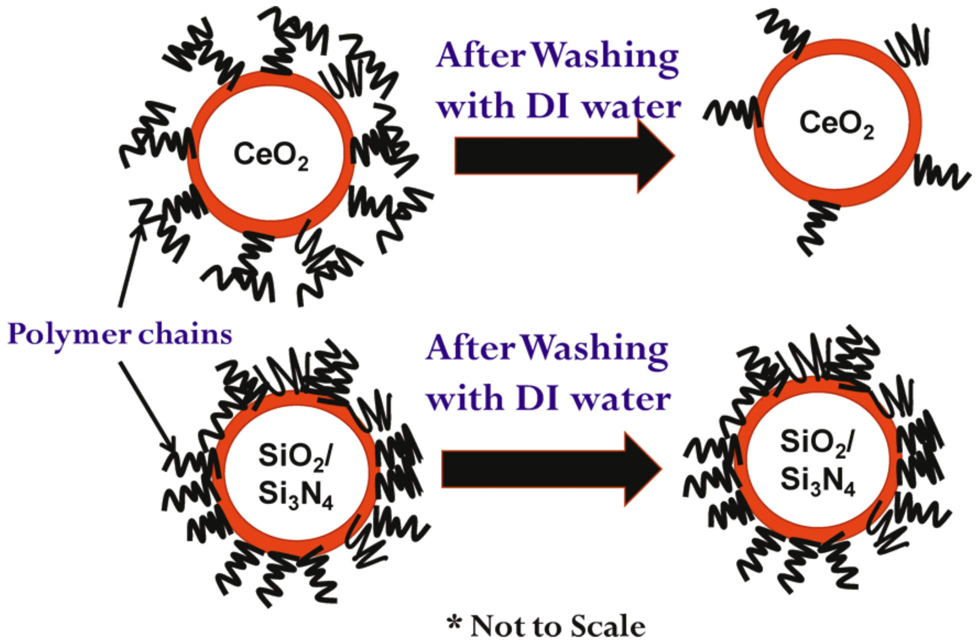
Ref: *Veera Dandu, PhD. thesis, Clarkson University*

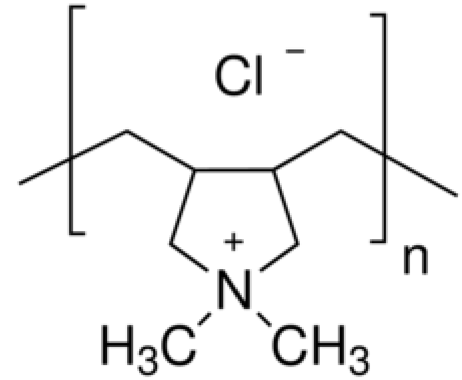
Effect of washing with water on adsorbed PA and proline at pH=5

No of times redispersed	PA (mg/g of solid) remaining on			Proline (mg/g of solid) remaining on		
	Si_3N_4	SiO_2	CeO_2	Si_3N_4	SiO_2	CeO_2
0	96	74	13	147	98	8
1	8	9	4	6	11	1
2	<1	<1	3	1	<1	1

- *Naresh Penta, PhD. thesis, Clarkson University*

Adsorption of polymers on particles



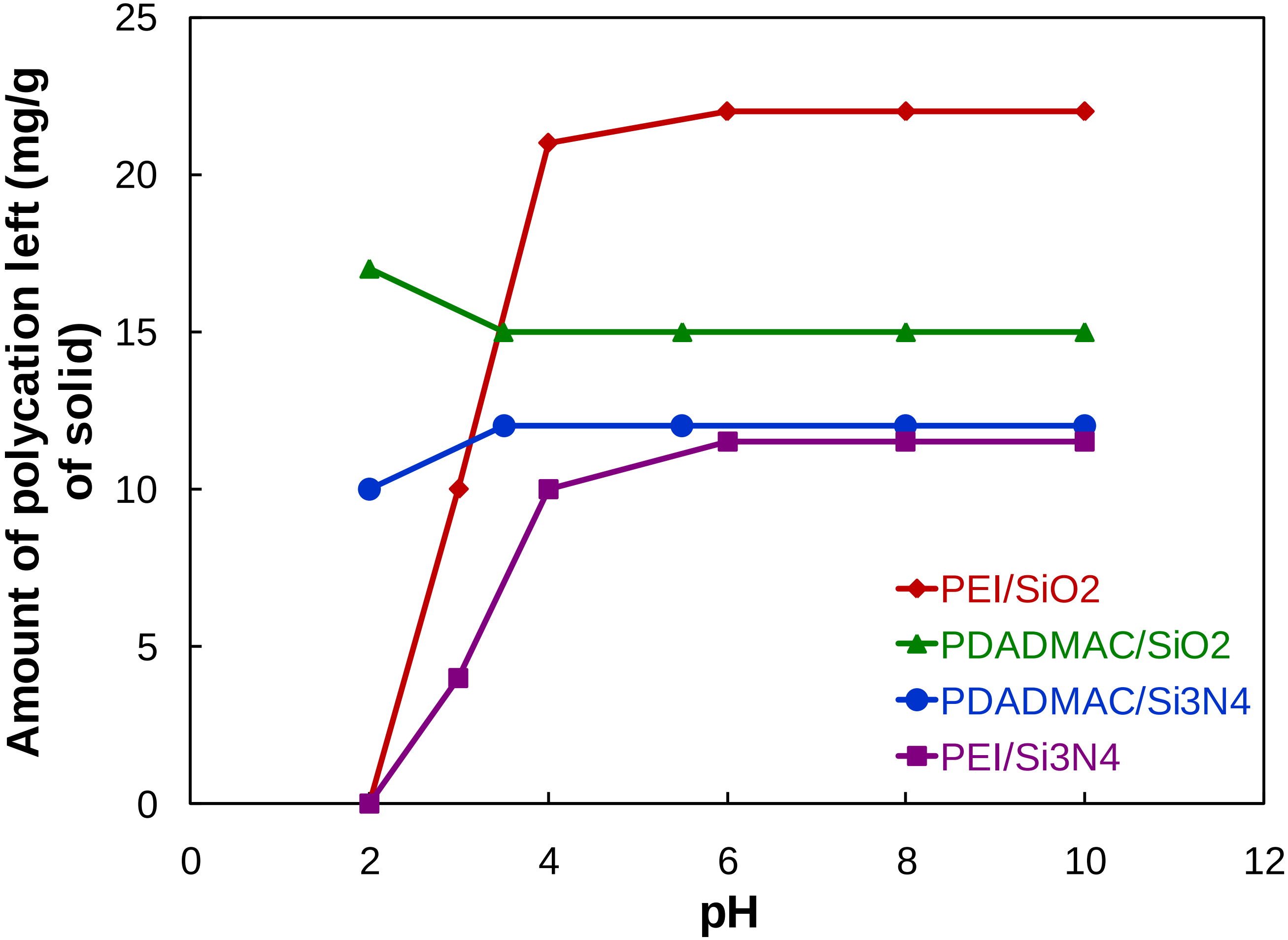


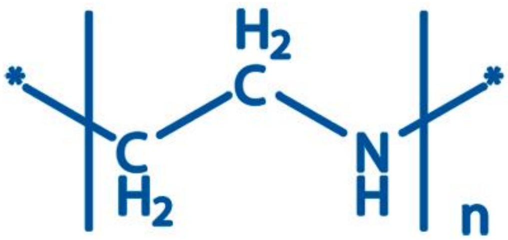
Structure of Poly diallyl dimethyl ammonium chloride (PDADMAC)

	Zeta Potential at pH 10		
	Bare	With 250 ppm PDADMAC	Modified particle dispersion
Ceria	-35	+56	+2
Silica	-60	+28	+21
Silicon Nitride	-38	+23	+24

- *Naresh K. Penta, P. R. Dandu Veera, and S. V. Babu. Langmuir 2011, 27, 3502–3510*

Adsorption of poly-cations on SiO_2 and Si_3N_4 surfaces



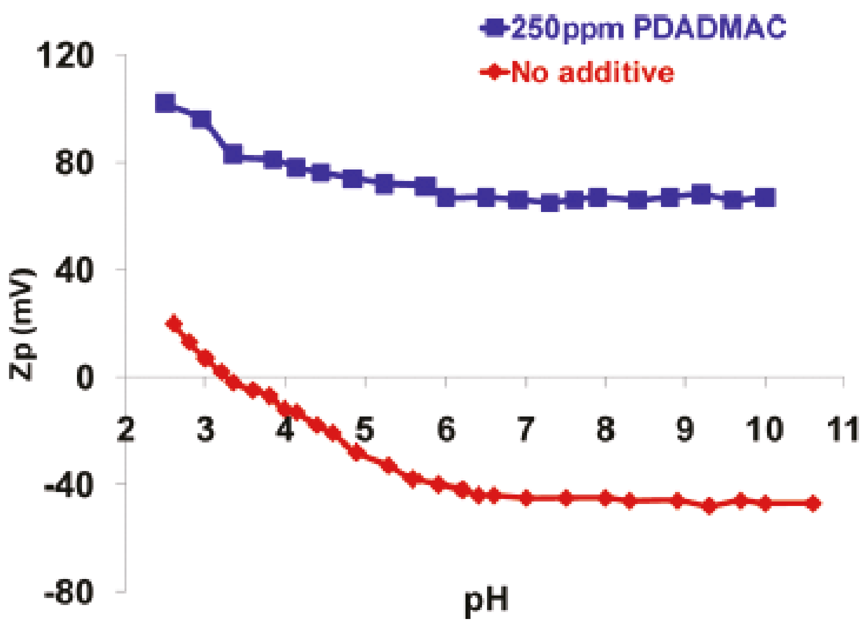


Polyethyleneimine (PEI)

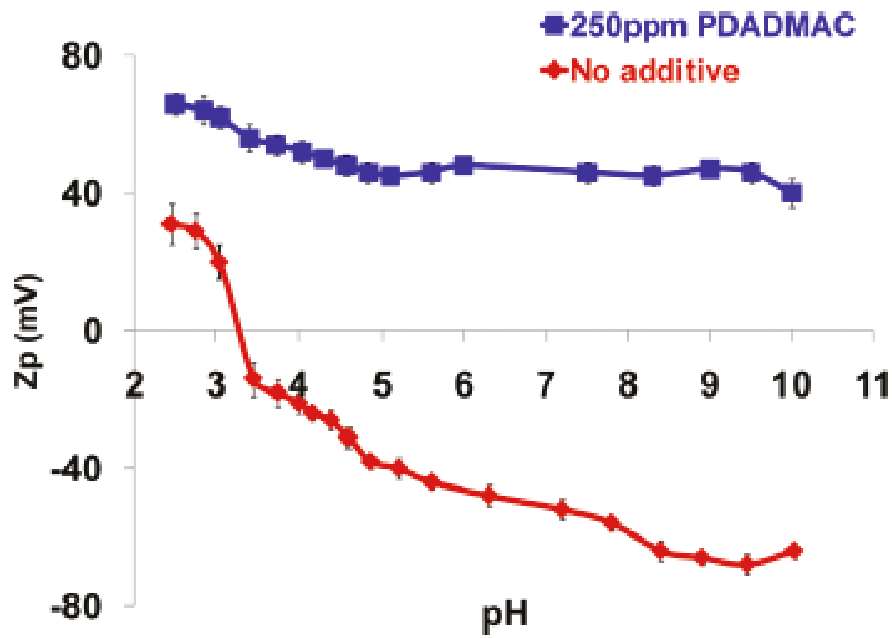
Amount of PDADMAC/PEI left on SiO_2 and Si_3N_4 surfaces after 2 washings with DI water at the respective pH values.

- *Naresh Penta, PhD. thesis, Clarkson University*

Adsorption of cationic polymers on poly-Si and IC-1000 pad surfaces



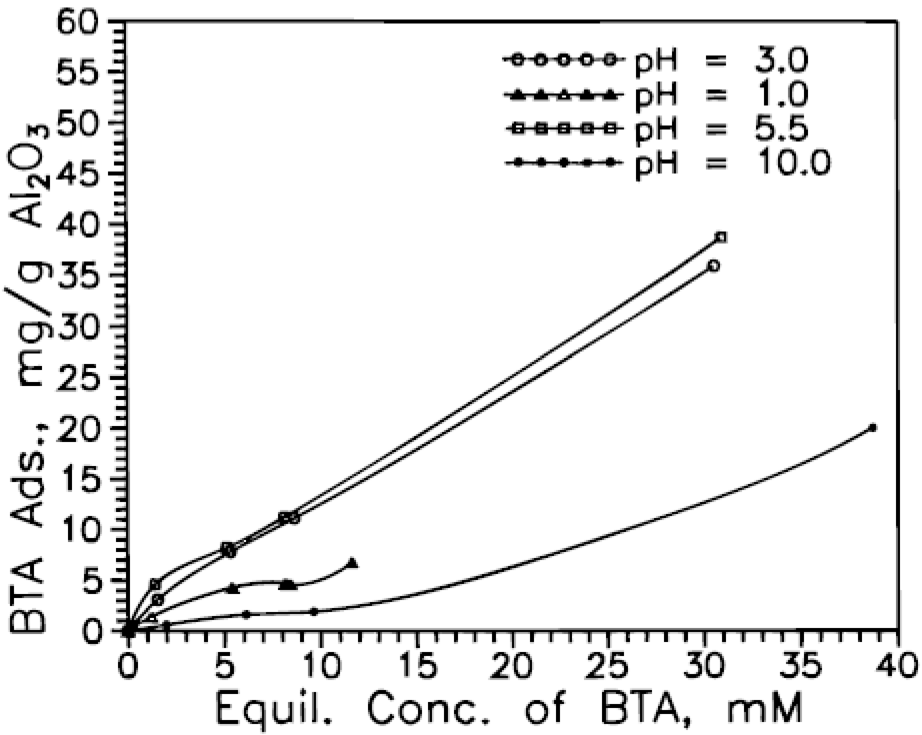
Zeta potentials of IC1000 pad in the absence and presence of 250 ppm PDADMAC.



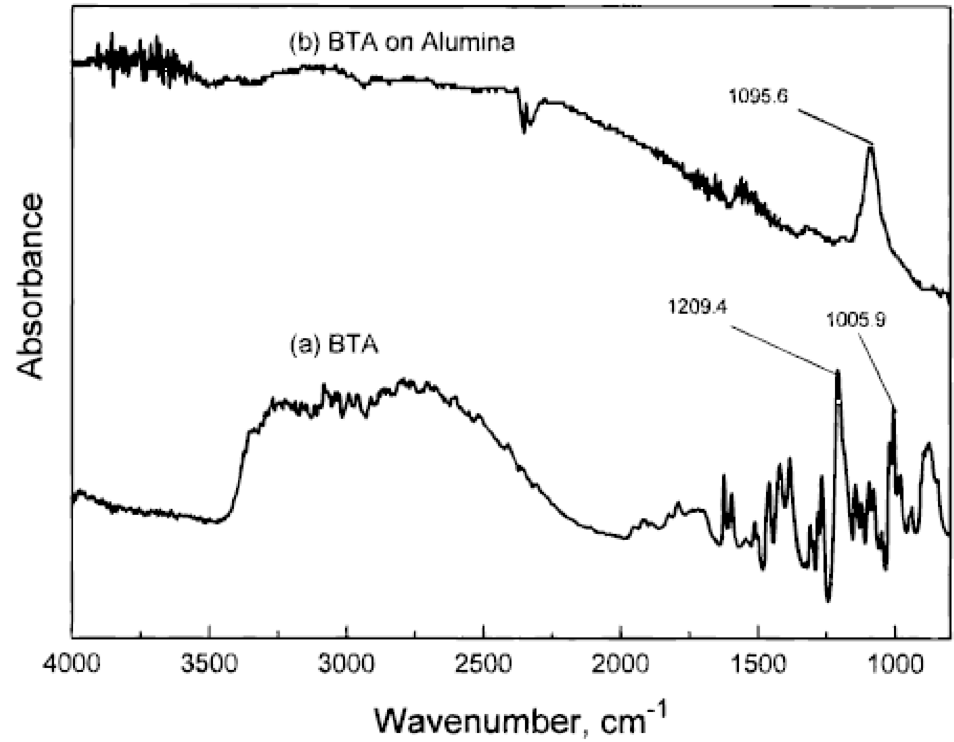
Zeta potentials of poly-Si films in the absence and presence of 250 ppm PDADMAC

- *Naresh K. Penta, P. R. Dandu Veera, and S. V. Babu. Langmuir 2011, 27, 3502–3510*

Adsorption of BTA on Alumina



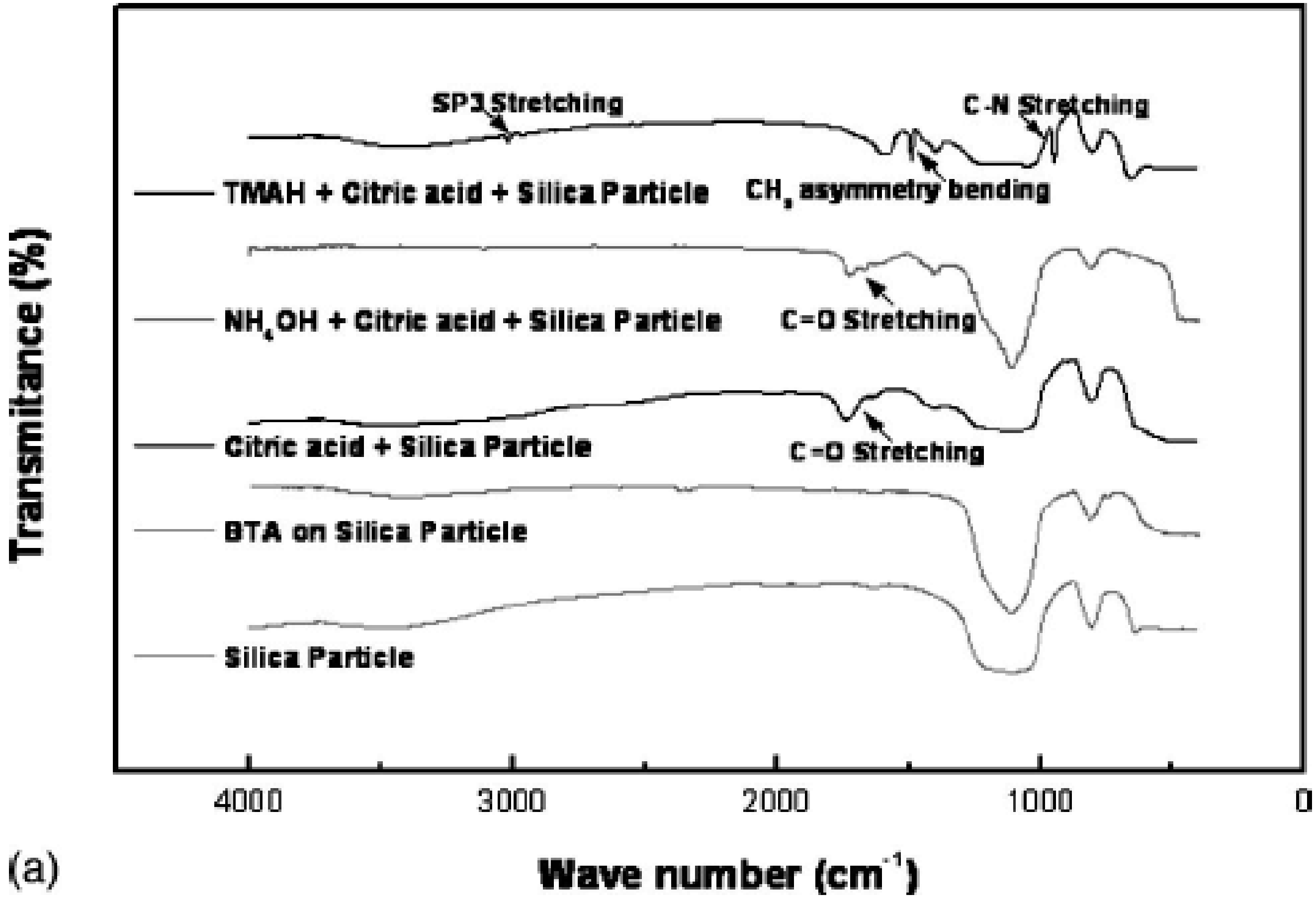
Adsorption isotherms of BTA on alumina particles at various pH's.
Changes in the adsorption of BTA can modify the surfaces and change the RRs.



FTIR Spectra:
C-H (stretching) 3053-3090 cm^{-1}
N-N (bending) 1209 cm^{-1}
N-H (stretching) 2800 cm^{-1}

- *Q. Luo,D. R. Campbell, and S. V. Babu. Langmuir **1996,** 12, 3563-3566*

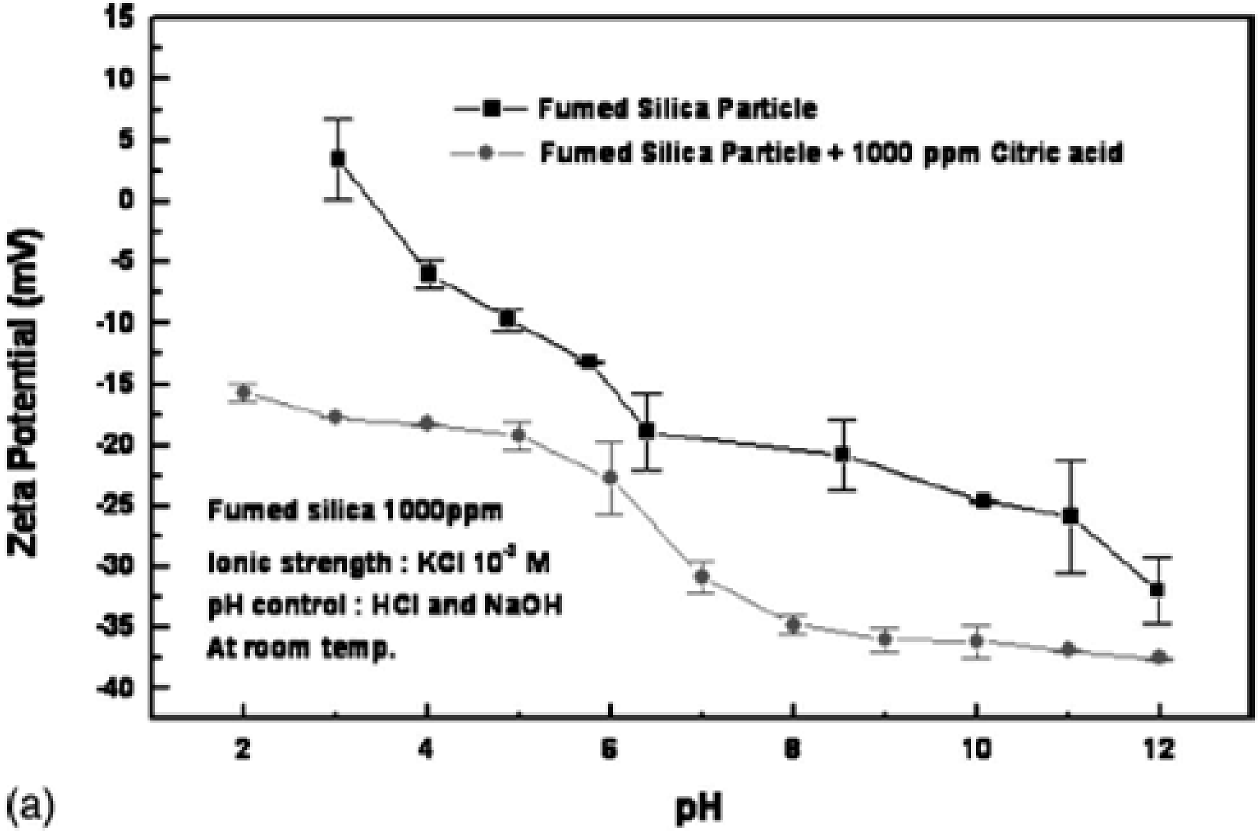
Binding of PCMP additives on silica surfaces



FTIR spectra of silica particles in various cleaning solutions

- *Yi-Koan Hong, Dae-Hong Eom, Sang-Ho Lee, Tae-Gon Kim, Jin-Goo Park and Ahmed A. Busnaina. J. Electrochem. Soc. 2004, Volume 151, Issue 11, Pages G756-G761*

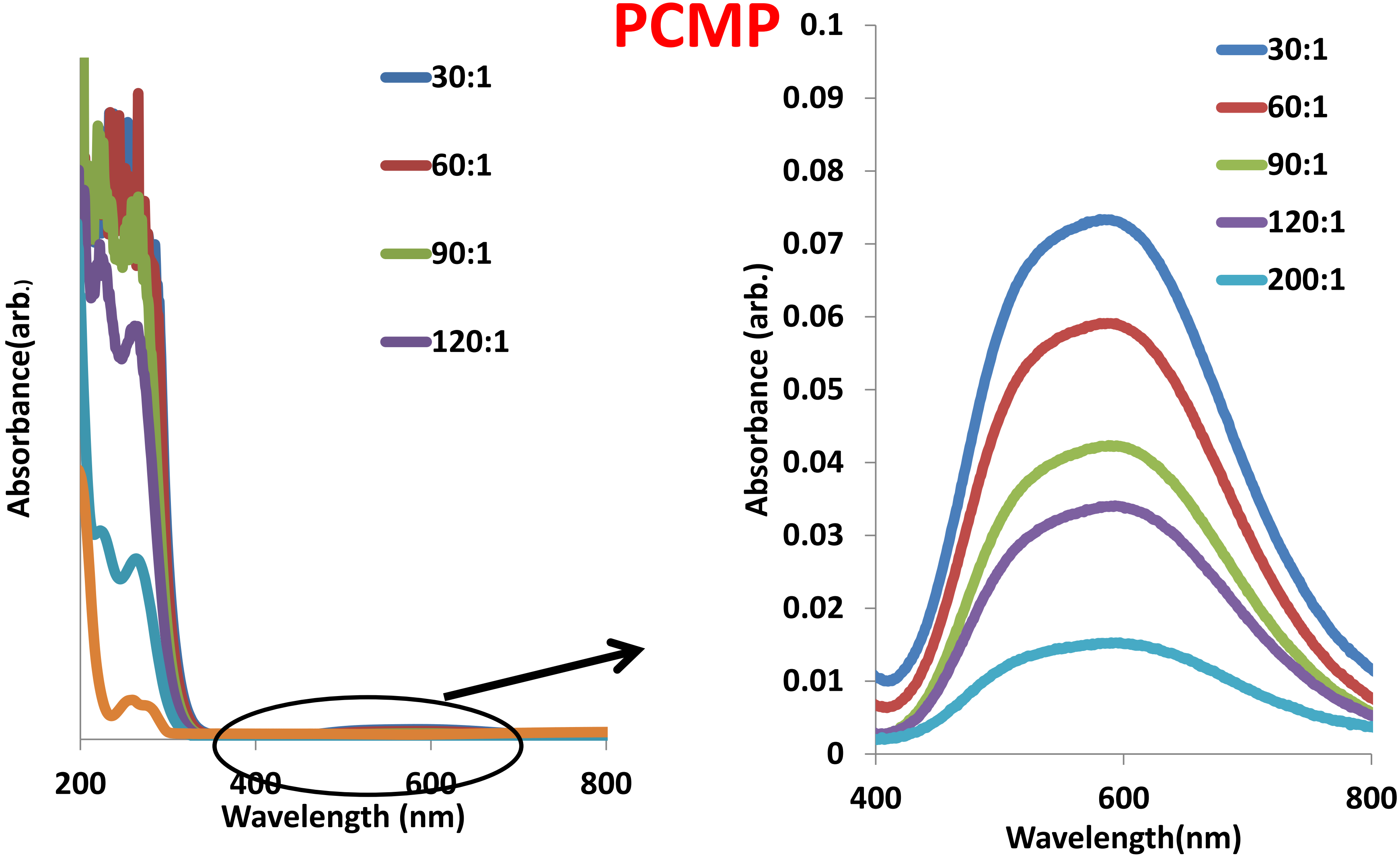
Zeta Potential of silica surfaces during PCMP cleaning



The zeta potential of (a) silica as a function of pH with and without the addition of citric acid.

- *Yi-Koan Hong, Dae-Hong Eom, Sang-Ho Lee, Tae-Gon Kim, Jin-Goo Park and Ahmed A. Busnaina. J. Electrochem. Soc. 2004, Volume 151, Issue 11, Pages G756-G761*

UV-Vis of spent 'Planar Clean' solution during Cu PCMP



Cu Oxide-Amine complex particles formed due to undercut process during PCMP.

- Tran et al., ECS Transactions, 44 (1), 2012, pg:565-571

Characteristics of GaAs processing waste streams

Source	Characteristics	pH	Total GaAs* (g/L)	Dissolved As (g/L)
Wafer polishing and backside polishing	Clear solution with alumina and SiO_2 particles. May be alkaline or acidic	10-11 6	3-5	1.8-2.4

* Solid GaAs Particulates and dissolved species (H_3AsO_3 (pH 2-9)), H_3AsO_4)

- http://www.semiconductor-today.com/features/Semiconductor%20Today%20-%20Management%20of%20arsenic-rich%20waste.pdf

Where do Ga and As end up during polish of GaAs?

pH	Element composition (μg/g)			
	Solids		Liquid	
	Ga	As	Ga	As
2	39.2	33.8	19.8	18.6
10	51.9	47	8.2	26

- John Matovu, Clarkson University, Unpublished data

Hazards associated with GaAs processing waste streams

Waste Stream	Possible Hazards	Hazard Minimization
Solid particles as dust	• Inhalation of dust	• Minimize dust generation through wet processing. • Ventilation and extraction of working area of grinders and saws. • Store waste in liquid slurry form in a closed container. • Wear Protective clothing , mask and gloves
CMP, grinding, cutting and lapping waste slurries	• Ingestion of GaAs. • Dermal Contact. • Contamination of ground water through improper disposal. • Ingestion of Arsenic. • Generation of arsine gas during polish and in waste container.	• Treat waste streams as hazardous waste and dispose of according to local and national regulations. • Wear protective clothing and gloves. • Avoid creating a reducing environment in waste slurry tank. • Maintain low pH in waste slurry to avert microbial activity.

- http://www.semiconductor-today.com/features/Semiconductor%20Today%20-%20Management%20of%20arsenic-rich%20waste.pdf

Effect of Aqueous Phase pH of Slurries on PH_3 Generation (30 sec polish of InP)

Slurry	Maximum PH_3 concentration (ppb) as a function of pH						
	2	4	6	7	8	10	12
0.3 M aq. H_2O_2 + 3 wt % silica	140 (34)	135 (4)	94 (10)	73 (16)	n.d.	n.d.	n.d.
0.3 M aq. H_2O_2 + 3 wt % silica + 0.08 M OA	109 (14)	87 (6)	15 (3)	n.d.	n.d.	n.d.	n.d.
0.3 M aq. H_2O_2 + 3 wt % silica + 0.08 M TA	120 (12)	69 (8)	26 (5)	11 (2)	n.d.	n.d.	n.d.
0.3 M aq. H_2O_2 + 3 wt % silica + 0.08 M CA	179 (15)	139 (10)	47 (3)	47 (4)	n.d.	n.d.	n.d.

Values in parentheses are standard errors of measurements; n.d. = not detected

CM-4 gas detector

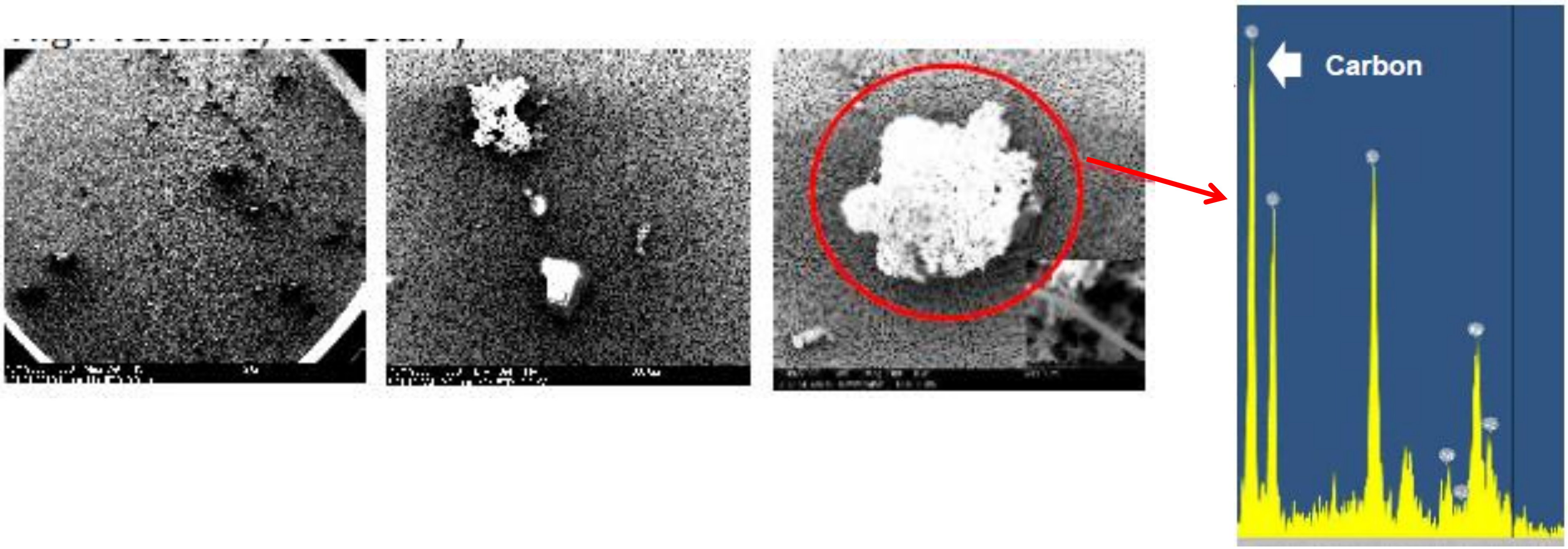
- John Matovu, Clarkson University, Unpublished data

Pad Debris

- Pad debris is often observed during polishing with in-situ conditioning.
- The polyurethane polishing pads possess both –COC- and -COOC - functional groups in the main chain structure that experience some degree of hydrolytic attack with usage.
- Alkaline media accelerates hydrolytic attack and in the presence of weak bases degrades the polyurethane more rapidly than neutral water.

- H. Lu et al. / Materials Characterization 49 (2002) 35–44

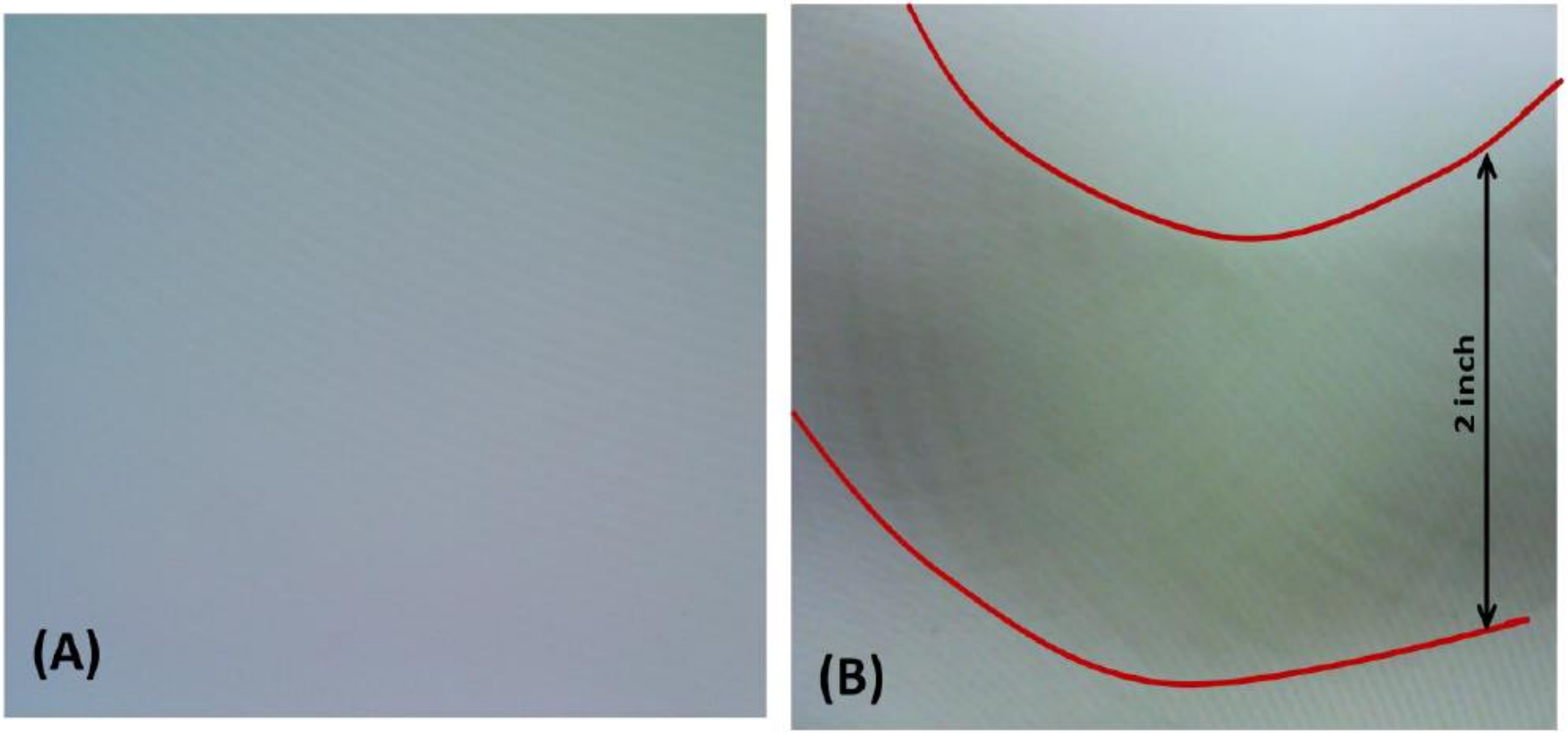
Pad Waste generated during CMP



- Particles in the effluent included slurry, agglomerates, and pad debris
- Carbon peak from SEM EDS identified pad debris

- http://www.confluense.com/publications/NCAVSCMPUGConfluense2009_final_Presentation.pdf

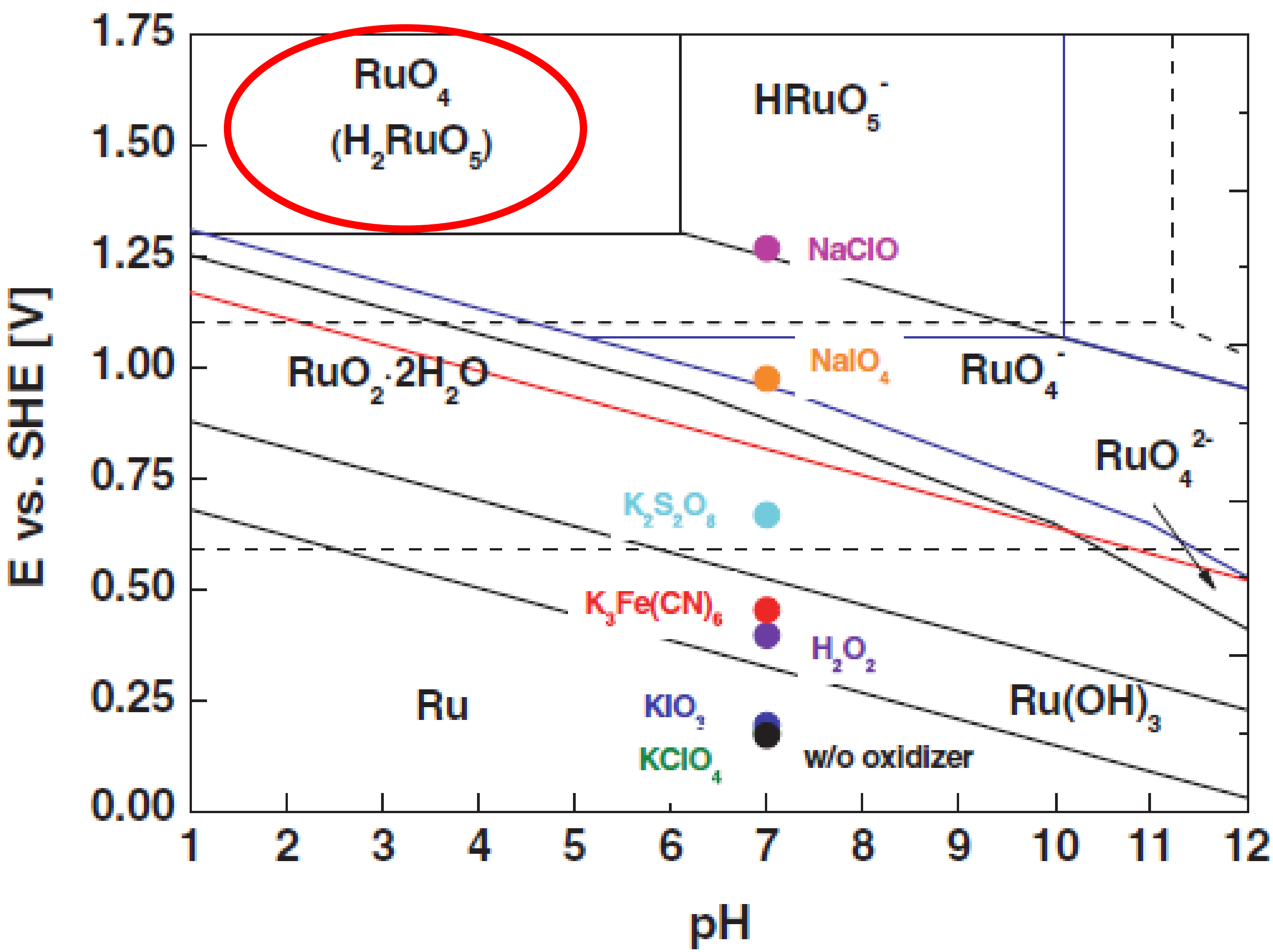
Pad staining during Ru polishing with KIO_4



Polishing pad (IC 1000) before (A) and after (B) polishing with a slurry containing 0.015 M KIO_4 + 5 wt% Silica at pH 6

- Brown Peethala., PhD. thesis. Clarkson University

Issues with Ruthenium CMP



RuO_4 :

Volatile, toxic and explosive

- Hao Cui, Jin-Hyung Park and Jea-Gun Park *ECS Journal of Solid State Science and Technology*, 2 (1) P26-P30 (2013).

Conclusions

Acknowledgements

NYSTAR
Empire State Development
Division of Science, Technology & Innovation

NYACOL
NANO TECHNOLOGIES, Inc.

DOW

IBM

G&P TECHNOLOGY

3M

FERRO

EVONIK
INDUSTRIES

Rhodia

intel

ATMI

CAMP

Clarkson
UNIVERSITY
defy convention

Thank You

Nanoparticles- Health issues related to size

Lung exposures

- Adverse inflammatory and fibrotic responses when compared with larger-sized particles of similar or identical composition at equivalent doses/mass concentrations.
- Studies on SiO_2 and TiO_2 nanoparticles indicate that surface reactivity of the particles influences the development of inflammatory and cytotoxic responses in the lung
- As the particle size is decreased, the proportion of atoms found at the surface is magnified relative to the proportion inside its volume.

Ref: David B. Warheit , Christie M. Sayes, Kenneth L. Reed, Keith A. Swain. *Pharmacology & Therapeutics 120 (2008) 35–42*

Safe-handling of nano-materials

1) Potential exposures mechanisms during the handling life cycle?

- *The four major routes of occupational exposure are the respiratory tract (i.e., inhalation exposure), the skin, eyes, and the gastrointestinal tract (via oral or inhalation exposures).*

2) Characterization and the following questions addressed: e.g. solid or liquid state, how dusty is the material, what is the size distribution, is the material water soluble?

3) Predominant route of exposure:

- *Particles Trapped and dispersed in the environment via air or moisture.*

Ref: David B. Warheit , Christie M. Sayes, Kenneth L. Reed, Keith A. Swain. *Pharmacology & Therapeutics 120 (2008) 35–42*