Complexation of III/V ions to nanoparticles involved in chemical mechanical polishing (CMP) process

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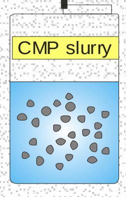
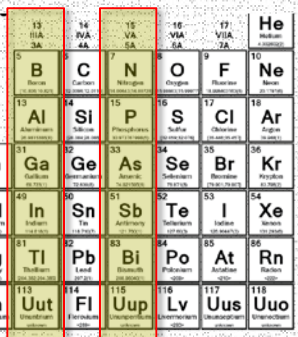
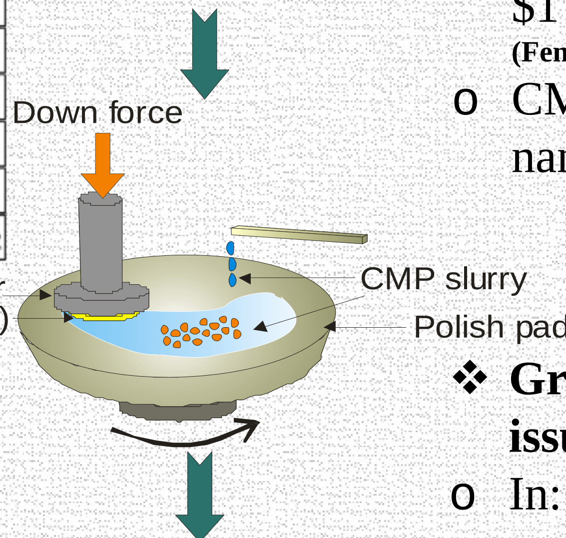
An industry case using "nanoparticles (NPs)": Chemical mechanical polishing(CMP)

Typical NPs:
SiO_2, CeO_2, Al_2O_3, etc.



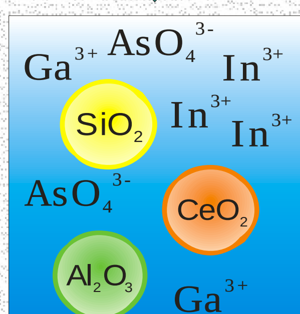
CMP slurry





e.g., III/V materials

Typical species:
GaAs, InP, GaN, etc.



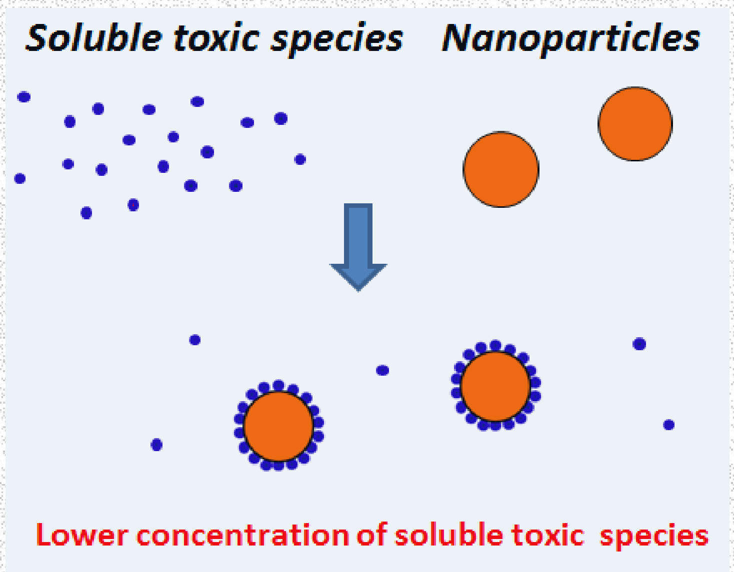
Post-CMP wastewater

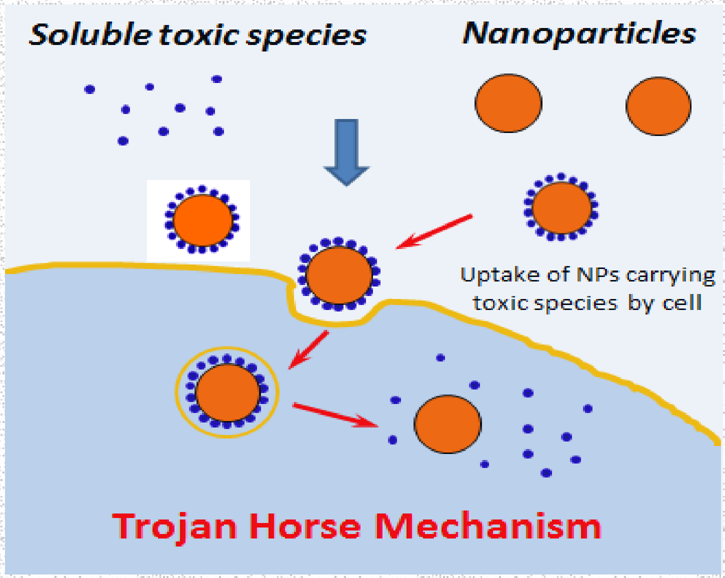
❖ **High global production of CMP NPs**
- Consumptions: **Si-5500 t/yr; Ce & Al-55 t/yr (Piccinno et al.,2012)**
- CMP nanoparticles constituted **nearly 60%** of the total \$1 billion worldwide market for nanopowders by 2005. **(Feng et al., 2006)**
- CMP is the **second largest** nano-market after nanocatalysts. **(Pitkethly,2002)**

❖ **Growing use of III/V materials and the potential issues**
- In: **0.95~20.05 ppb** in groundwater near a semiconductor manufacture (0.01ppb in background). **(Chan, 2006)**
- Ga: **~27ppm to ~2000ppm** in polishing wastewater. **(Torrance et al., 2010)**
- As: **1800-2400 mg/L** dissolved As in polishing waste stream. **(Torrance and Keenan, 2009)**

Research hypothesis and question

❖ Concerns on the interaction of III/V ions with CMP NPs





Toxicological study in collaboration with **Prof. Reyes Sierria at University of Arizona** and **Prof. Robert Tanguay at Oregon State University .**

- This work serves as ***the first step*** toward testing the hypothesis that CMP NPs and III/V ions lead to a synergetic ecological risk via "Trojan Horse mechanism", by answering the question: **What is the expected quantity of III/V ions that can be adsorbed to CMP NPs in aquatic environment?**

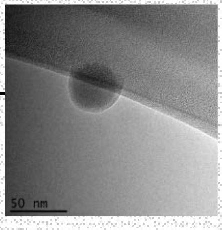
ARIZONA STATE UNIVERSITY

Materials for experiment

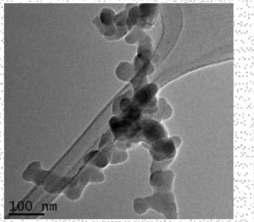
- Four model CMP slurries were obtained directly from Cabot Microelectronics.
  - ❖ Manufacture provided information

Slurry name	nanoparticle concentration	nanoparticle size (nm)	pH	pH adjusting agent
Colloidal silica	3 wt%	50-60	2.5-4.5	acetic acid <1%
Fumed silica	5 wt%	120-140	10	KOH <1%
Ceria	1 wt%	60-100	3-4	---
Alumina	3 wt%	80-100	4.5-5.0	nitric acid <1%

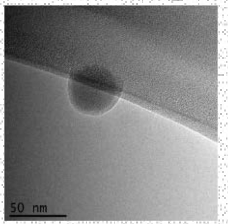
Colloidal SiO_2



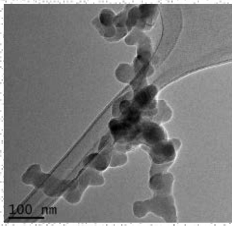
Fumed SiO_2



Colloidal SiO_2



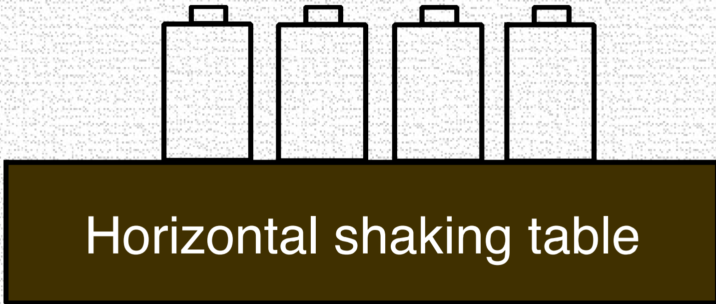
Fumed SiO_2



- More information on CMP NPs can be found from:

- Speed, David; Westerhoff, Paul; et al. *"Physical, chemical, and in vitro toxicological characterization of nanoparticles in chemical mechanical planarization suspensions used in the semiconductor industry: towards environmental health and safety assessments."* **Environmental Science: Nano (2015), 2, 227-244, DOI: 10.1039/C5EN00046G .**
- Bi, X., Reed, R. B., & Westerhoff, P. (2015). Control of nanomaterials used in chemical mechanical polishing/planarization slurries during on-site industrial and municipal biological wastewater treatment. In Baalousha, M. & Lead, J. R.(Eds.), ***Characterization of nanomaterials in complex environmental and biological media*** **(PP247-265). Waltham, MA: Elsevier. ISBN :9780080999487.**

Adsorption experiment method



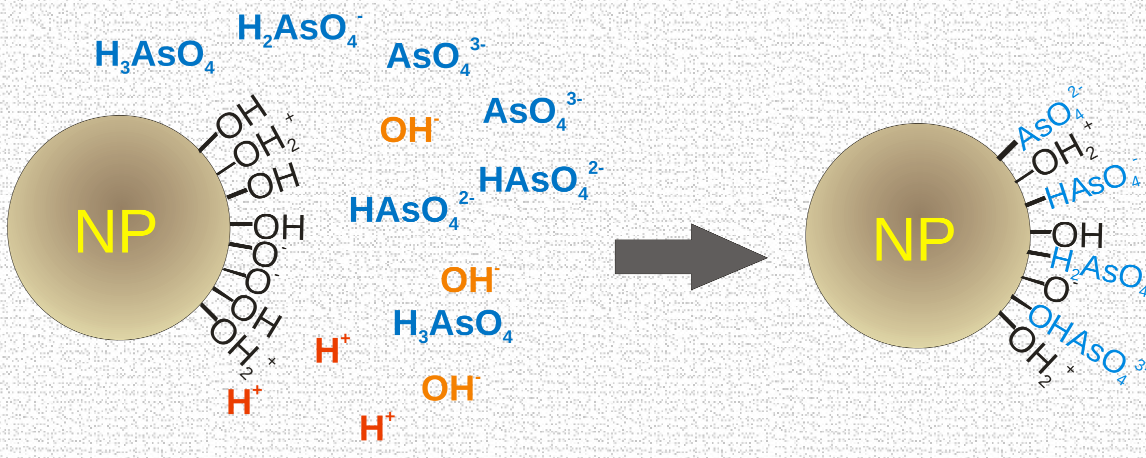
- In(III), Ga(III) or As(V) ion stock solutions were spiked into NP solutions.
- pH was controled by HCl and NaOH.
- In background of 0.1 M NaCl.
- Shaking for 3 days.

- Millipore centrifugal ultrafiltration device
- 30 Da regenerated cellulose membrane embedded.

- Filtrate (solution going through membrane) is analyzed by ICP-MS (Thermo X series 2).

The formulation of surface complexation model

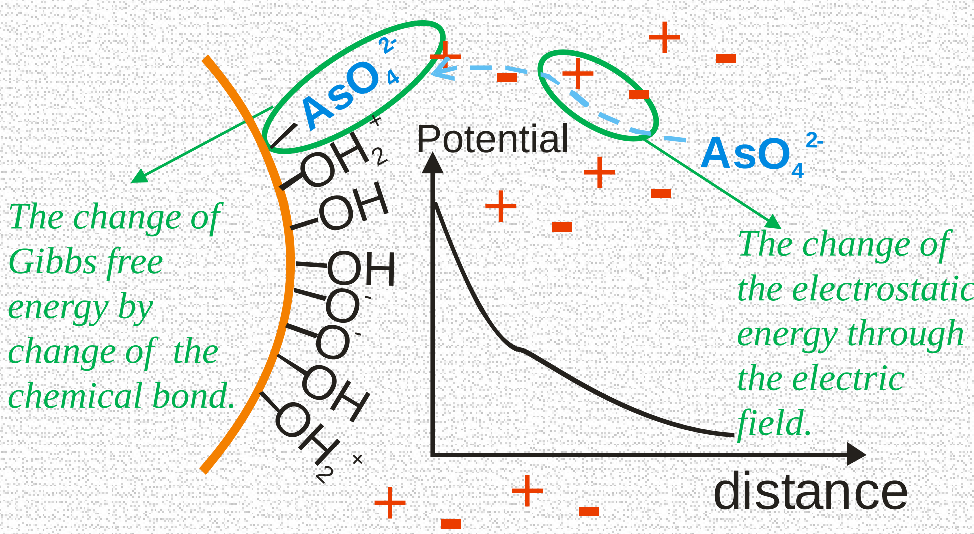
-for the case of AsO_4^{3-} ions



A *surface complexation model* assumes adsorption occurs on specific sites on particle surface, i.e., -OH, forming surface ligands for different As(V) species.

$$NP-OH + AsO_4^{3-} + H^+ \rightleftarrows NP-AsO_4^{2-} + H_2O$$

$$K_{app} = \frac{\left[NP-AsO_4^{2-}\right]}{\left[NP-OH\right]\left[AsO_4^{3-}\right]\left[H^+\right]}$$



$$K_{app} = K_{int} \exp\left(-\frac{ZF\Phi}{RT}\right)$$

- K_{app}: *Apparent constant*
- K_{int}: *Intrinsic constant*
- $\exp\left(-\frac{ZF\Phi}{RT}\right)$: *Coulomb term*

The formulation of surface complexation model

-for the case of AsO_4^{3-} ions

$$H_3AsO_4 \rightleftarrows 3H^+ + AsO_4^{3-} \quad K^1_{As}$$

$$H_2AsO_4^- \rightleftarrows 2H^+ + AsO_4^{3-} \quad K^2_{As}$$

$$HAsO_4^{2-} \rightleftarrows H^+ + AsO_4^{3-} \quad K^3_{As}$$

$$NP-OH_2^+ \rightleftarrows NP-OH + H^+ \quad K^1_S$$

$$NP-OH \rightleftarrows NP-O^- + H^+ \quad K^2_S$$

$$NP-OH + (AsO_4^{3-} + H^+) \rightleftarrows NP-AsO_4^{2-} + H_2O \quad K^1_C \cdot C^{-2}$$

$$NP-OH + (AsO_4^{3-} + 2H^+) \rightleftarrows NP-HAsO_4^- + H_2O \quad K^2_C \cdot C^{-1}$$

$$NP-OH + (AsO_4^{3-} + 3H^+) \rightleftarrows NP-H_2AsO_4 + H_2O \quad K^3_C$$

$$NP-OH + AsO_4^{3-} \rightleftarrows NP-OHAsO_4^{3-} \quad K^4_C \cdot C^{-3}$$

$$AsTOT = \sum species\ containing\ As$$

$$NPconc \cdot SSA \cdot SSD / N_A = \sum_x NP - x$$

Known

Determined by fitting zeta potential data.

Adsorption-determined parameters

$$AsAds\% = f(Kc1,\ Kc2,\ Kc3,\ Kc4,\ SSA,\ pH)$$

→ Fit experimental data.

K^1_{As} = 20.6; K^2_{As} = 18.36; K^3_{As} = 11.6; from Drever 1997.

AsTOT: total As(V) ion concentration, 0.1 mM in this work.

NPconc: total NP concentration, 500mg/L as Ce or Al in this work.

SSD: surface site density, in nm^{-2}.

SSA: specific surface area, in m^2kg^{-1}.

NP-x: any site on NP surface.

Outcome impacts

- Information to semiconductor industry: The Adsorption to CMP NPs can be a critical fate of III/V ions in wastewater.

Ion	pH condition	Colloidal SiO_2	fumed SiO_2	CeO_2	Al_2O_3
Ga(III)	acidic	●	●	●	●
	neutral	●●	●●	●●	●●
	basic	●	●	●●	●
As(V)	acidic	◐	◐	●◐	●●
	neutral	○	◐	●	●
	basic	○	○	◐	◐
In(III)	acid	○	○	◐	◐

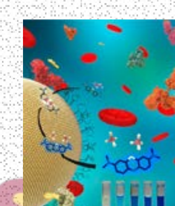
● Significant adsorption
◐ Slight adsorption
○ No adsorption

- Surface complexation model provides information on adsorption mechanism and guides the industry to predict III/V ion and NP interactions under different conditions (e.g., pH).
- This study provides the critical groundwork for the next research on the "synergetic" risk assessment for CMP NPs and III/V ions.

Bioassays for multiple trophic level toxicity studies.



Colorimetric detection of NP reactivity.



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- All other coworkers and colleagues at ASU.