Investigation of Speciation in III-V Wet Etching to Mitigate Hazardous Product Formation

(*Task Number: 425.049)*

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Other Researchers:

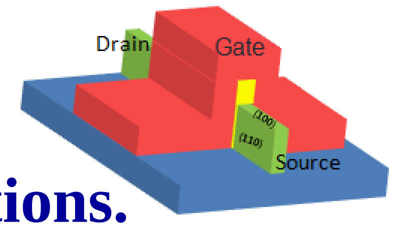
- **Tim Corley, Hydrology and Water Resources**

Cost Share (other than core ERC funding):

-

Objectives

- III-V materials allow for manufacturing beyond the limits of silicon.
- Predict the species produced by wet etching III-V semiconductors.
  - Use thermodynamics of liquid phase solutions.
  - Vary pH, molarity, solution chemistry.



FinFET

- Validate speciation at select process conditions.
  - Measure gas and liquid phases.
  - Mass balance on Ga and In.
    - Total
    - Species
  - Scale bench top experiments to full wafer.
  - Start with aqueous solutions of HCl and H_2O_2.

ESH Metrics and Impact

Marker	Max 30 day average	Source
Total Toxic Organics	1.37 mg/l	40 CFR 469.24
Arsenic	0.83 mg/l	40 CFR 469.24
pH	6-9	40 CFR 469.24

Compound	Exposure	Hazard
In_2O_3, $In(OH)_3$	Inhalation via Occupational Exposure	Lung Cancer, Pulmonary Alveolar Proteinosis, Emphysema
AsH_3	Chronic Exposure >0.05 ppm	Anemia, Cardiovascular Disease, Peripheral Neuropathy

Cummings, Kristin J. et al. "Indium Lung Disease." Chest 141.6 (2012): 1512–1521. PMC. Web. 28 Mar. 2015.

Arsine; MSDS No. P-4565-J [online]; Praxair: Danbury Ct, March 23, 2015

III-V Wet Etching

- **Define concentrations of all reaction products as function of processing conditions including waste disposal.**
  - **$[H_2O_2]$ = 0.0001 – 8 M**
  - **[HCl] = 0.01-2 M**
- **Scale species concentrations in gas and liquid phase to identify potential situations that do not meet regulations.**
  - **Limitations of current hydride sensors.**
  - **Reports of 97-99% recovery of indium using MRT gels.**

Approach

- **Use thermodynamics to identify the species to expect in the gas and liquid phases for different pairings of III-V material and etching chemistry.**

- **Close a mass balance on the etching process by measuring total masses of group III and V atoms in gas and liquid.**

- **Measure partitioning of species in gas and liquid for different pairings of III-V material and etching chemistry.**
  - **Especially important to measure In in aqueous phase to determine whether both chloride and hydroxide present.**

Thermodynamic Modeling

- **Software packages used to predict speciation.**
  - **PHREEQCi**
    - **Designed by USGS for aqueous systems.**
  - **STABCAL**
    - **Commercial**
- **Both software packages make use of thermodynamic databases or manually entered parameters.**
- **Validate with experiments.**
- **Use to guide selection of techniques to measure species concentration.**

Example HCl and H_2O_2 System

- HCl (0.01 – 1.76 M) and H_2O_2 (1.0 E-4 – 8 M) based solutions are commonly used for etching III-V materials.
  - Characterized by a redox potential in the range of 0.70 – 1.1 V.
- Potential-pH (Pourbaix) diagrams were constructed for the following conditions.

  [In] = 1.0 E-5 M; $[Cl^-]$ = 0.01 or 1.76 M

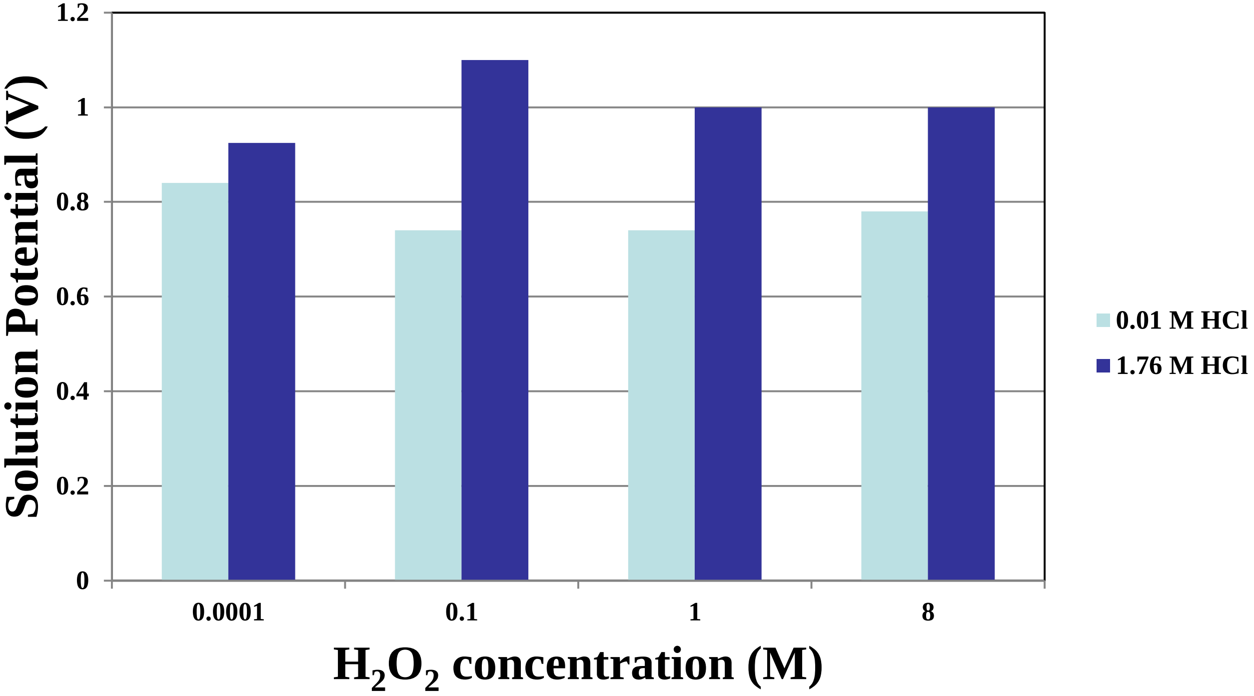
  pH range of -1 to 7

  Potential range of 0 – 2 V
- Distribution-potential diagrams were constructed for the following conditions.

  [In] = 1.0 E-5 M; pH=2 or -0.24

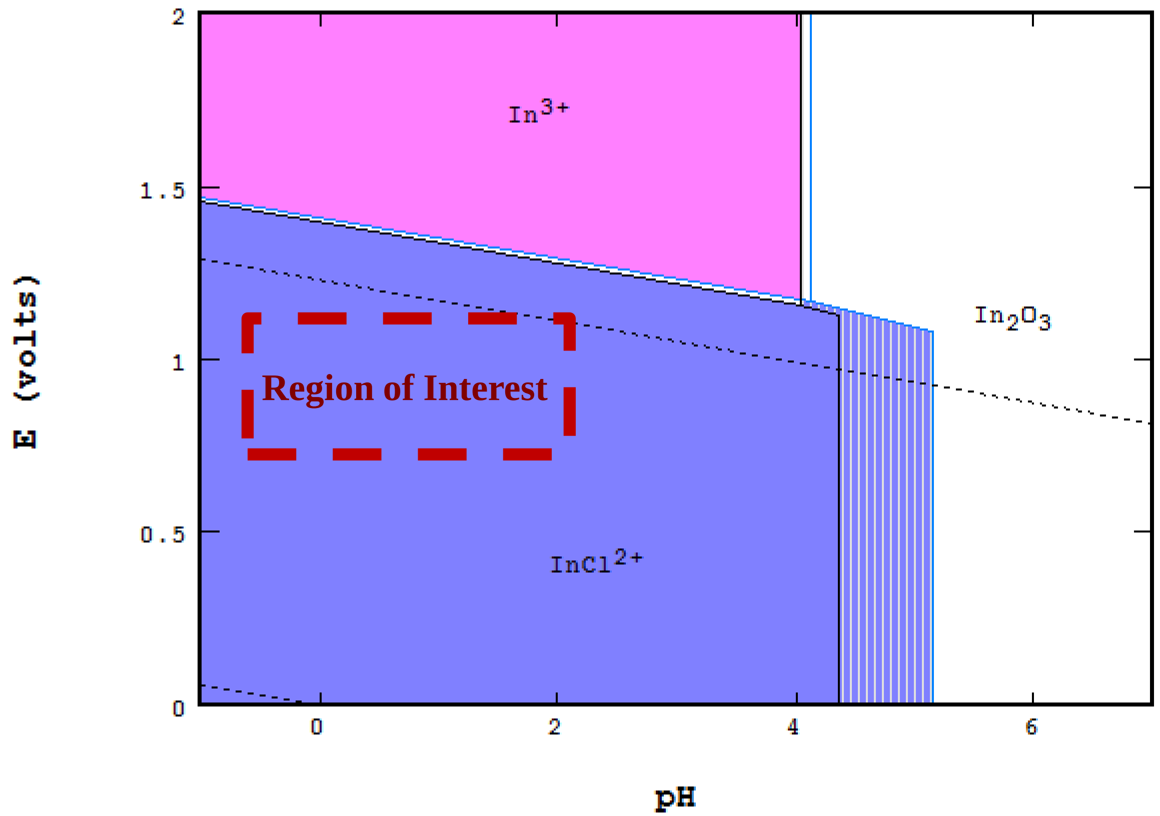
  Potential range of 0 – 2 V

Solution Potential as a Function of H_2O_2 Concentration



Potential-pH Diagrams

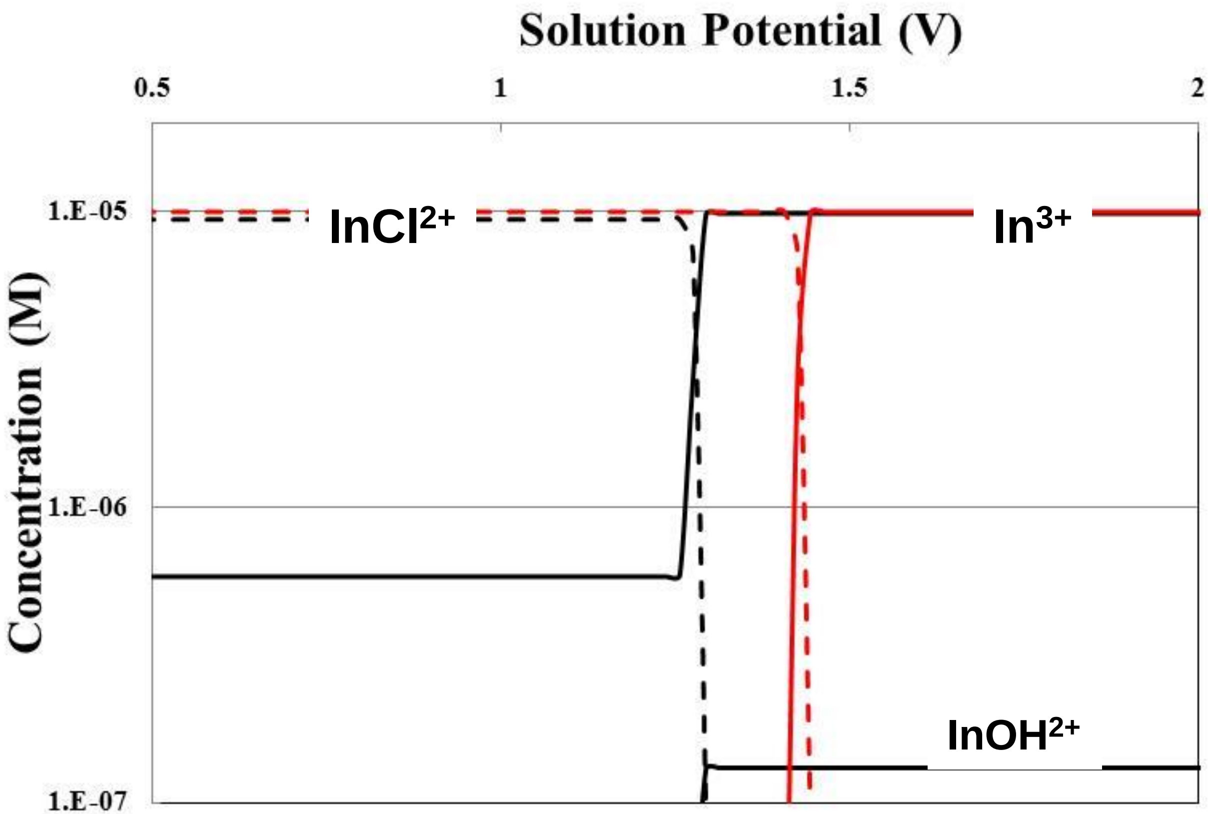
In (10^{-5} M) – Cl^- (0.01 or 1.76 M) – Water System



Comparison

Increase in Cl^- increases the stability region of $InCl^{2+}$

Distribution of Indium Species as a Function of Solution Potential

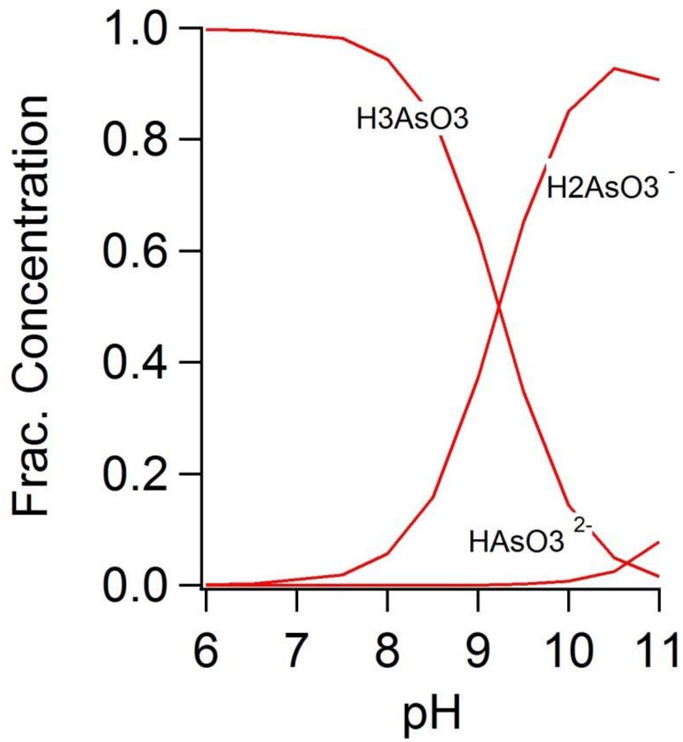


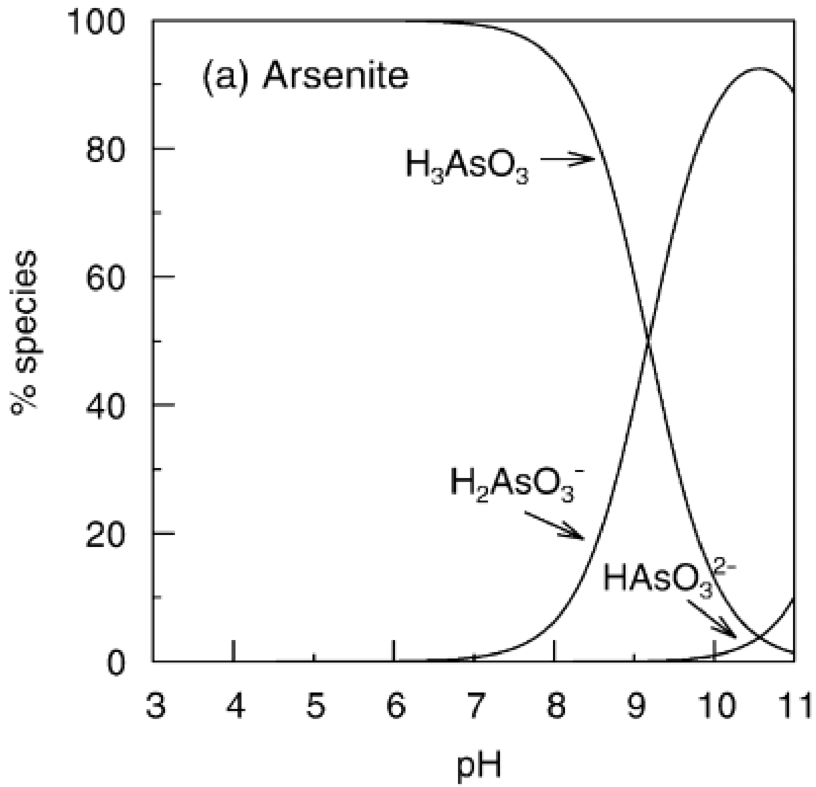
$[In]_t = 10^{-5}$ M

Black
0.01 M Cl$^-$
pH = 2

Red
1.76 M Cl$^-$
pH = -0.24

Arsenic Distribution in PHREEQCi





- **Good agreement between PHREEQCi and diagram from literature.**

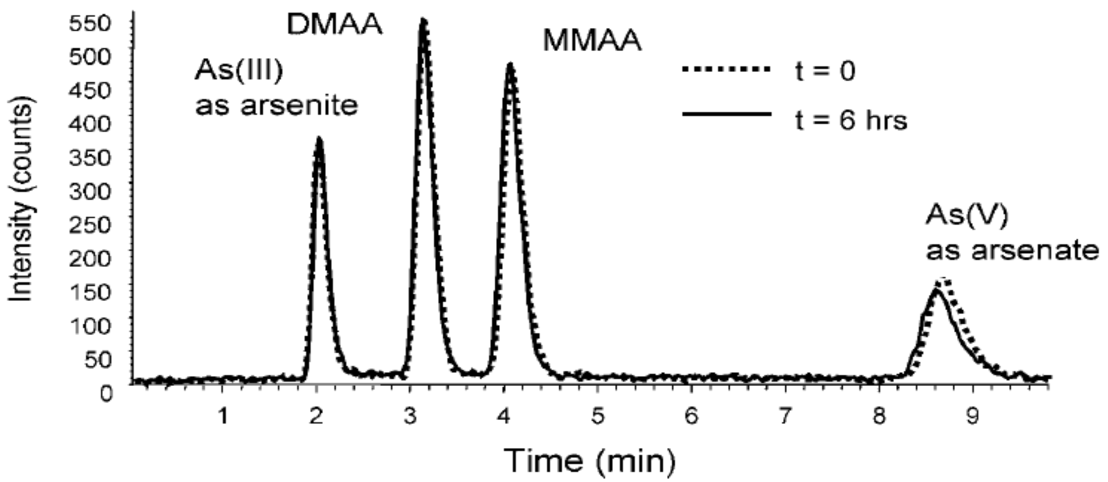
Smedley, P.l, and D.g Kinniburgh. "A Review of the Source, Behaviour and Distribution of Arsenic in Natural Waters." Applied Geochemistry 17.5 (2002): 517-68. Web.

Species Monitored in Vapor and Liquid Phases

Equipment	Purpose	Detection Range
Differentially Pumped Mass-Spec	Vapor Phase Detection	> 1 ppt sensitivity
ICP-MS	Liquid Phase Detection	< 10 µg/l
ICP-OES	Liquid Phase Detection	> 10 µg/l

Measurement Example

Compound	Phase	Detection Method
Aqueous As(III), As(V) species	Liquid	HPLC-ICP-MS
AsH_3	Vapor	ICP-MS FTIR: 2115.2, 906.75, 1126.42, 999.22 cm^{-1}



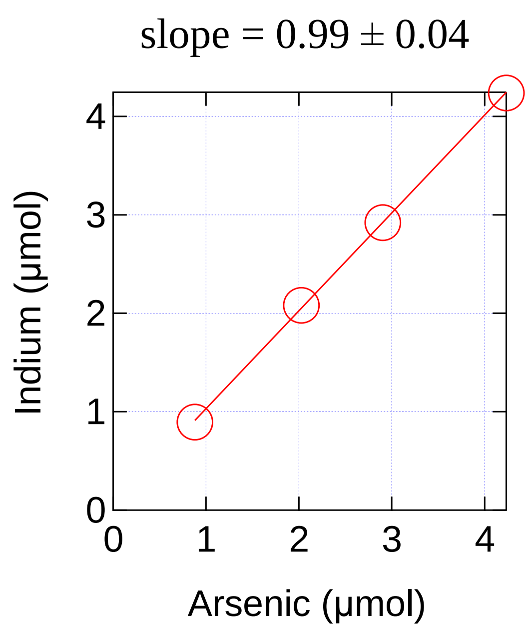
Day, Jason A et al. "A Study of Method Robustness for Arsenic Speciation in Drinking Water Samples by Anion Exchange HPLC-ICP-MS." *Analytical and Bioanalytical Chemistry* 373.7 (2002): 664-68. Web.

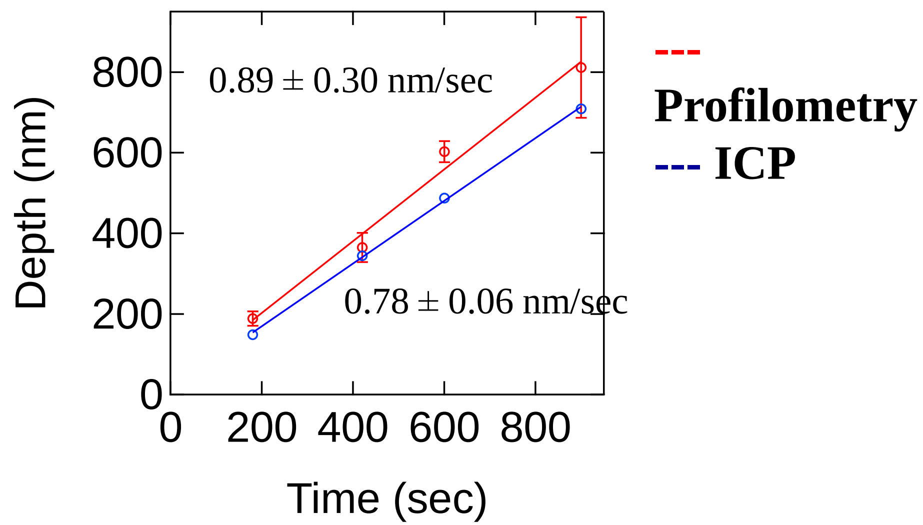
Total Mass Balance Experiment

- **InAs (100)**
  - **1x1 cm^2 samples patterned and unpatterned**

- **Etching rate**
  - **Unpatterned**
    - **Timed submersion in aq. [HCl]=0.01 M and [H_2O_2]=0.1 M.**
    - **Aliquots removed at discrete time intervals and analyzed by ICP-MS.**
    - **No gas phase data.**
  - **Patterned**
    - **Etch, remove photoresist, and measure amount etched by profilometry.**

Total Mass Balance and Etching Rate





1:1 In to As stoichiometry in solution suggests all species remain in liquid phase.

InAs(100) etching rate (nm/s) based on profilometry and ICP-MS agrees.

Conclusions

- **$InCl^{2+}$ species stable in solution based on thermodynamic model at concentrations and solution potentials of interest.**

- **Closed total mass balance on InAs(100) etching reaction based on close comparison of profilometry and ICP-MS etching rate data.**

- **In/As = 1:1 in solution suggests all species remain in liquid.**

Future Work

- **Develop thermodynamic calculations.**
  - **Expand databases for use in both PHREEQCi and STABCAL.**
  - **Replicate simulations in both sets of software to ensure continuity between programs.**
  - **Extend to binary systems**

- **Start speciation experiments.**
  - **Complete differentially-pumped mass spec to measure gas phase species.**
  - **Develop liquid phase separation procedures for III-V etching products.**

Industrial Interactions and Technology Transfer

Industrial liaisons:

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