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

(Task Number: 425.049)

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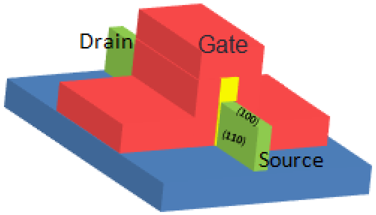
- **Tim Corley, Hydrology and Water Resources, UA**

Objectives

- ***Significance*. Address safety and disposal of III-V materials that could enable faster *n*-type transistors that use less power.**

- **Predict the species produced by wet etching III-V semiconductors.**
  - **Use thermodynamic modeling.**
  - **Vary pH, molarity, solution chemistry.**



FinFET

- **Validate models at select process conditions.**
  - **Measure both gas and liquid phases.**
  - **Mass balance on group III (Ga and In) and V (As and Sb).**
    - **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

Identify Products from III-V Wet Etching

- **Define concentrations of relevant reaction products as function of processing conditions including waste disposal.**
  - **Wet Etching Parameters**
    - **$[H_2O_2] = 0.0001 – 8$ M**
    - **$[HCl] = 0.01-2$ M**
    - **Waste treatment may form hazardous species**

- **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.**

Speciation Gives Insight Into Kinetics

- **Selectivity for different III-V compounds**
  - **Total mass balances show selectivity**
    - **Role of changing group III vs group V atoms**

- **Etching Rate and Reaction Rate**
  - **Total Mass Balance can determine etching rate**
  - **Reaction Rate derivable from Etching Rate**
  - **Determine reaction order**

$$R' = k_0 e^{-\frac{E}{RT}} A_{\text{III-V}}^{m} [\mathrm{H}^{+}]^{n} [\mathrm{HOOH}]^{p}$$

Thermodynamics Guides Measurement

- Use thermodynamics to predict species in 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.

Complete Speciation May Not Be Necessary

- Feedback from industrial liaisons indicates that a complete study of the speciation products is not necessary at this point.

- Initial phase project will focus on liquid/gas partitioning and broad categories of species
  - Hydroxides vs Chlorides

- Initial phase will also examine simple chemistries such as HCl and H_2O_2

Software for Calculations

- **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

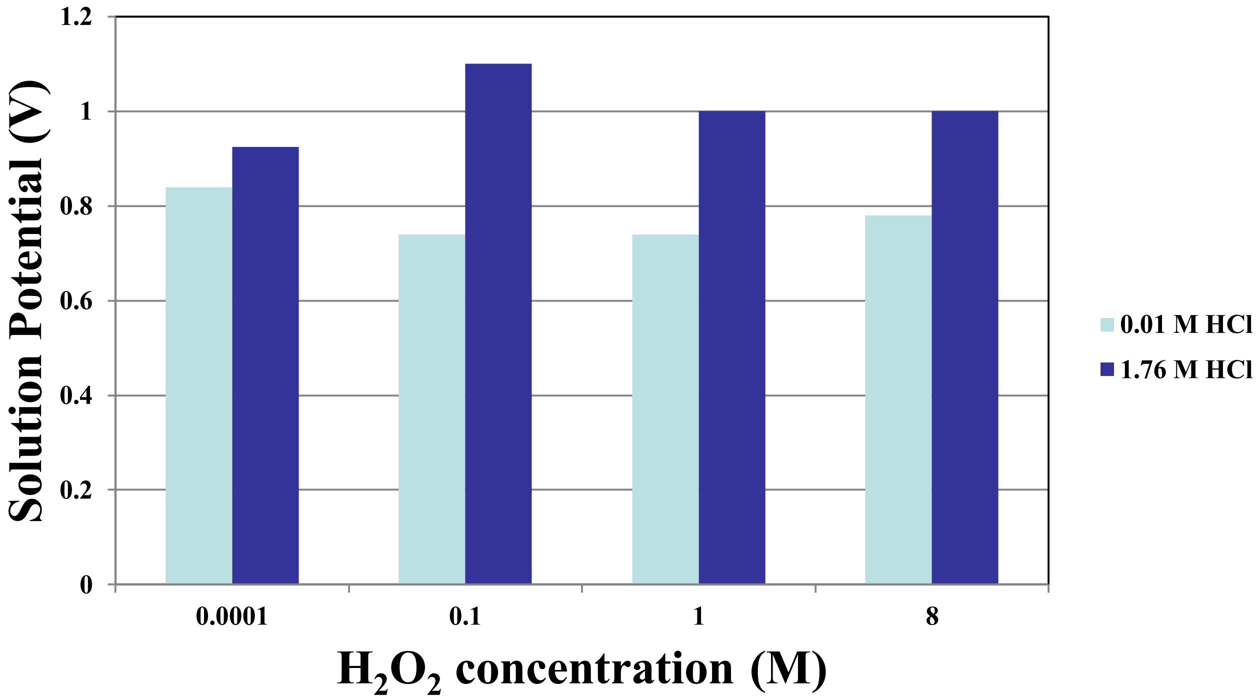
  pH range of -1 to 7

  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

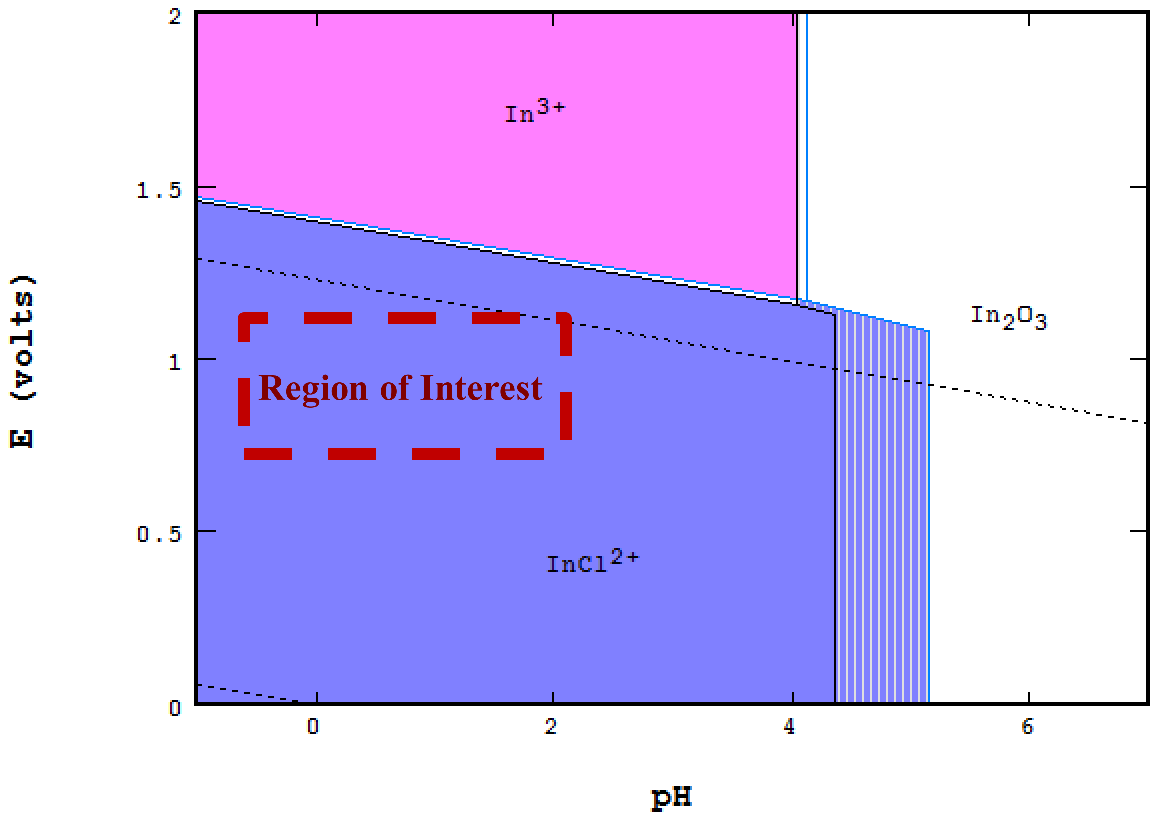
  Potential range of 0 – 2 V

Solution Potential as a Function of H_2O_2 Concentration



Potential-pH Diagrams

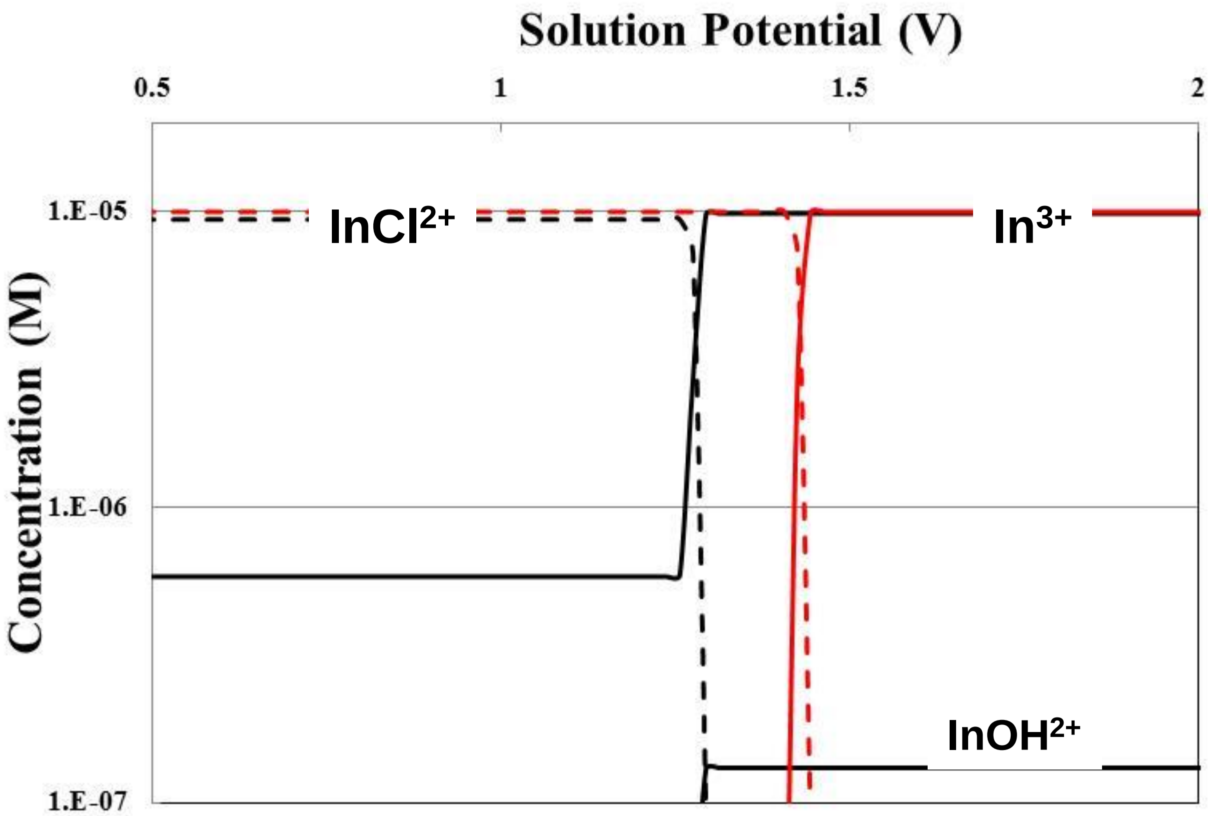
In (10^{-5} M) – Cl^- (0.01 or 1.76 M) – Water System



Comparison

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

Distribution of Indium Species as a Function of Solution Potential

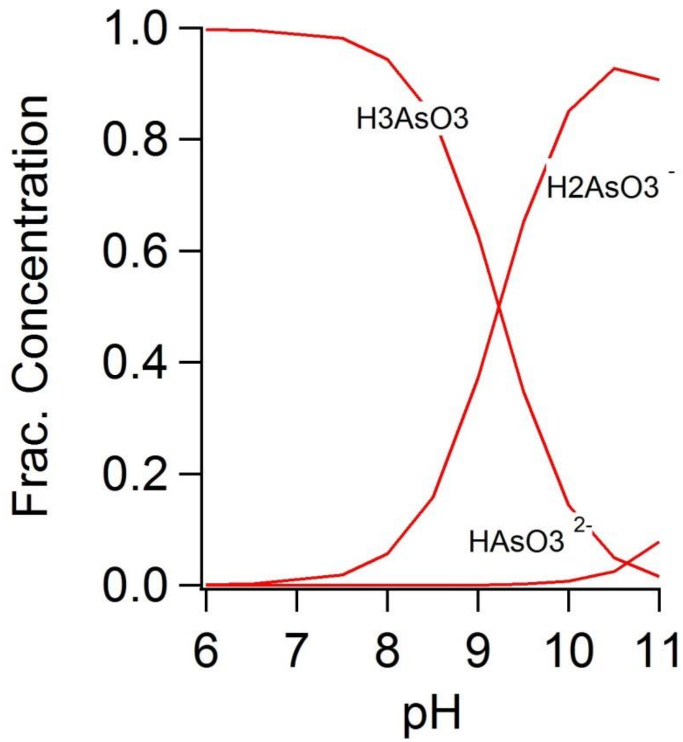


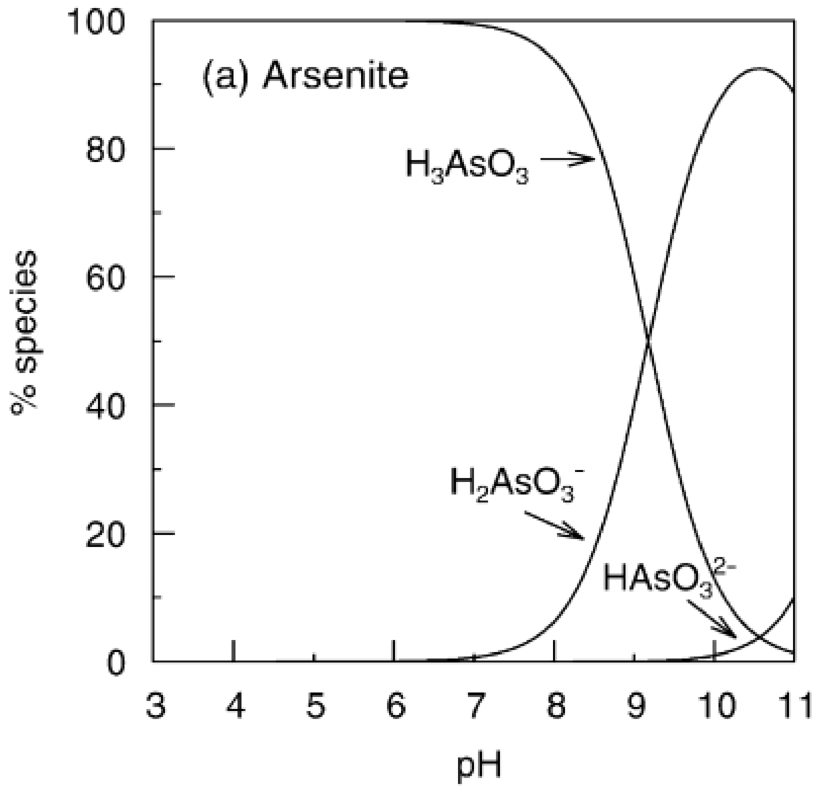
$[In]_t = 10^{-5}$ M

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.**

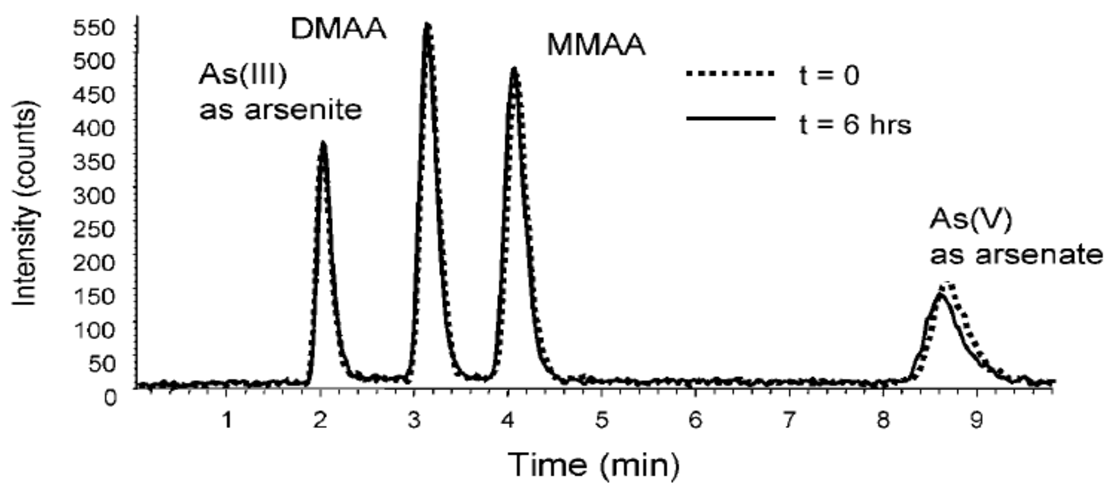
Smedley, P.l, and D.g Kinniburgh. "A Review of the Source, Behaviour and Distribution of Arsenic in Natural Waters." Applied Geochemistry 17.5 (2002): 517-68. Web.

Measurement Techniques in Vapor and Aqueous 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

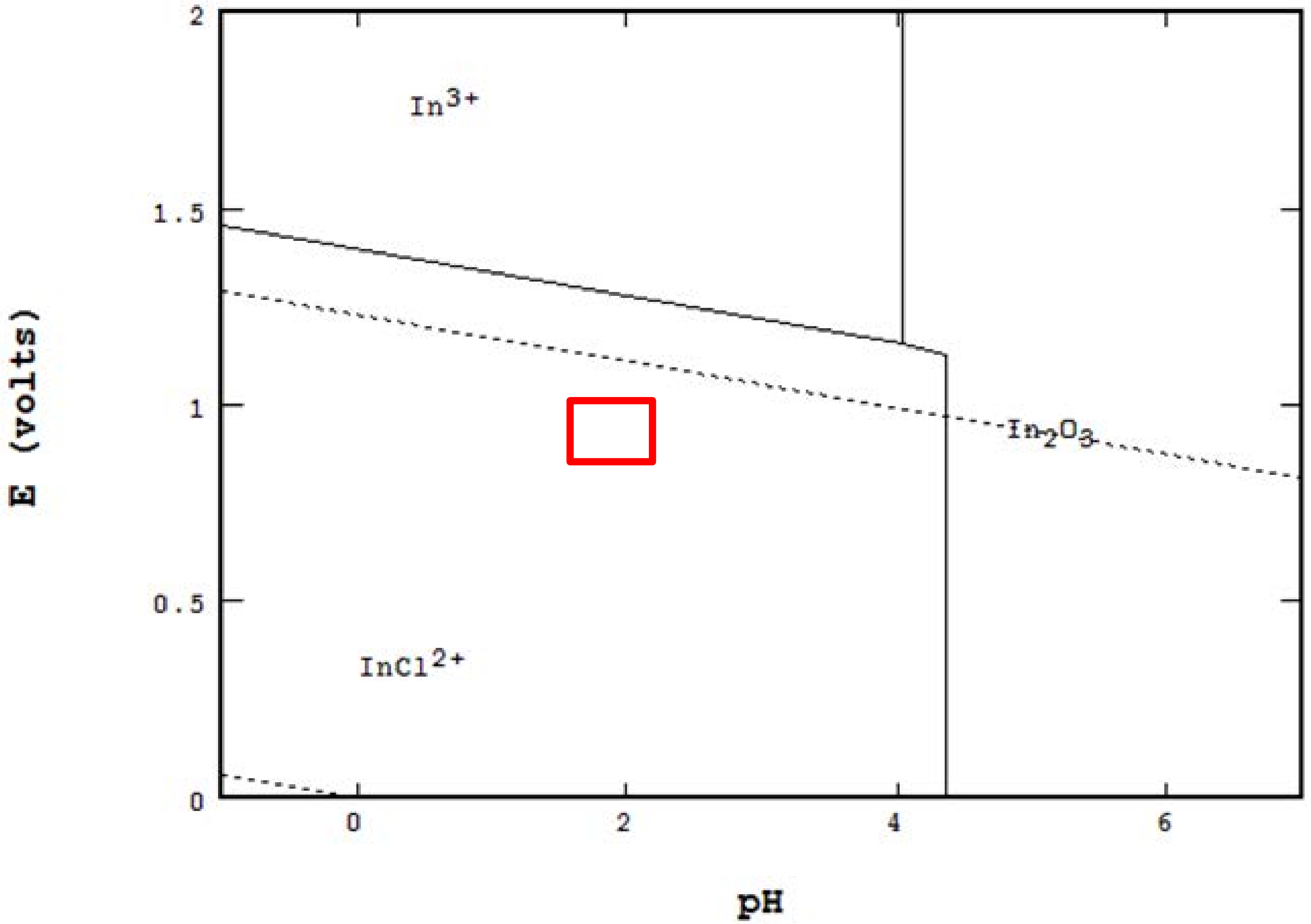
Measure Different Oxidation States

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}

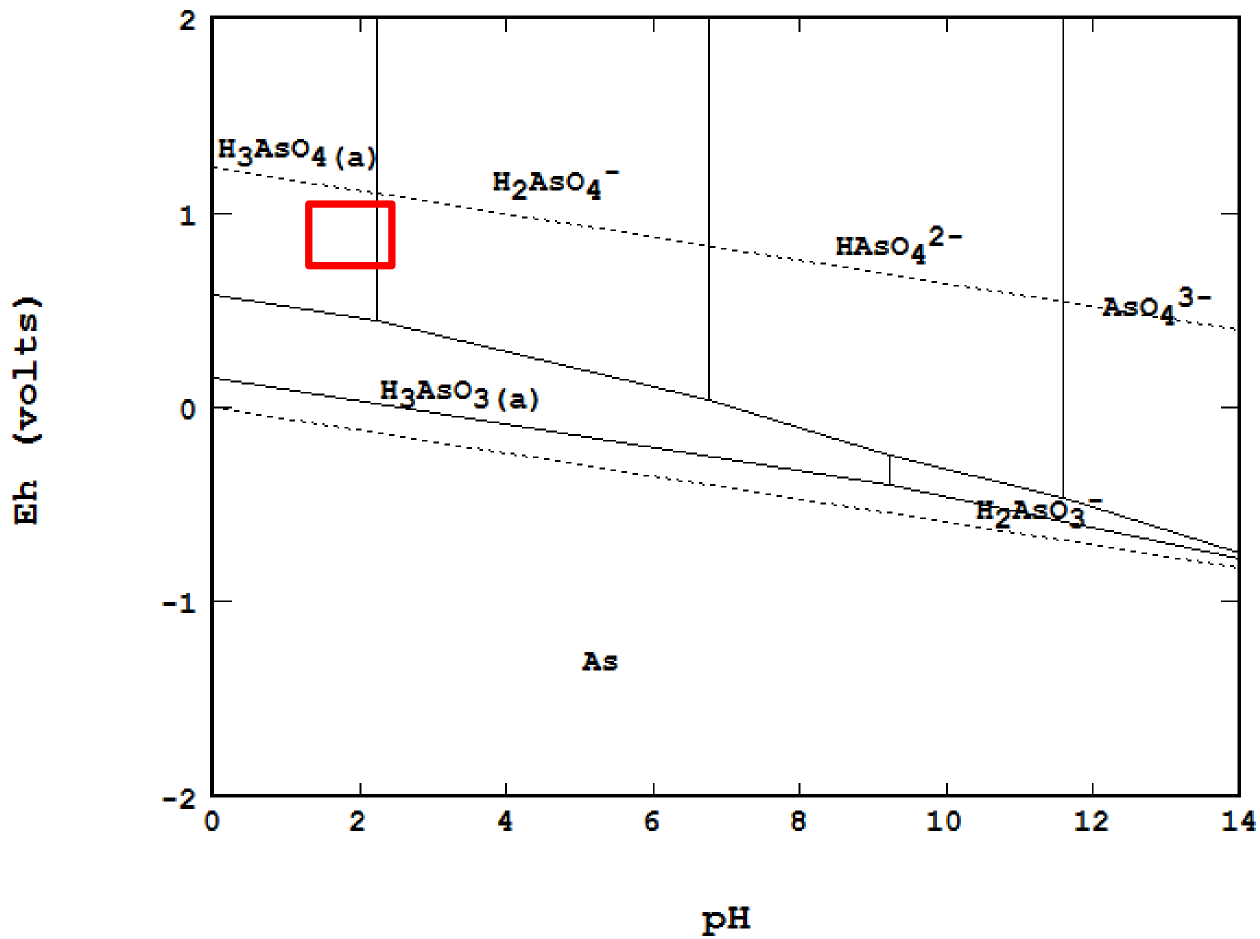


Day, Jason A et al. "A Study of Method Robustness for Arsenic Speciation in Drinking Water Samples by Anion Exchange HPLC-ICP-MS." *Analytical and Bioanalytical Chemistry* 373.7 (2002): 664-68. Web.

Aqueous Indium Expected



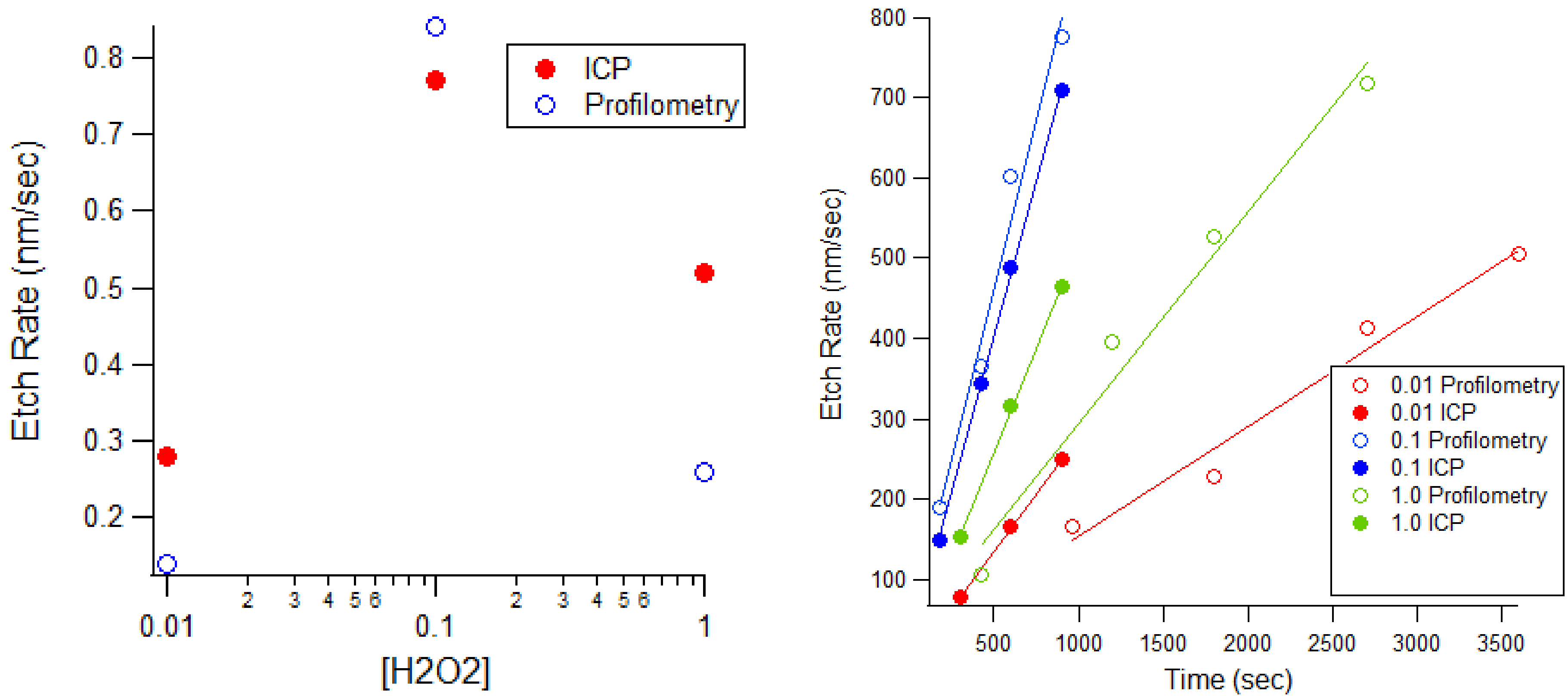
Aqueous Arsenic Expected



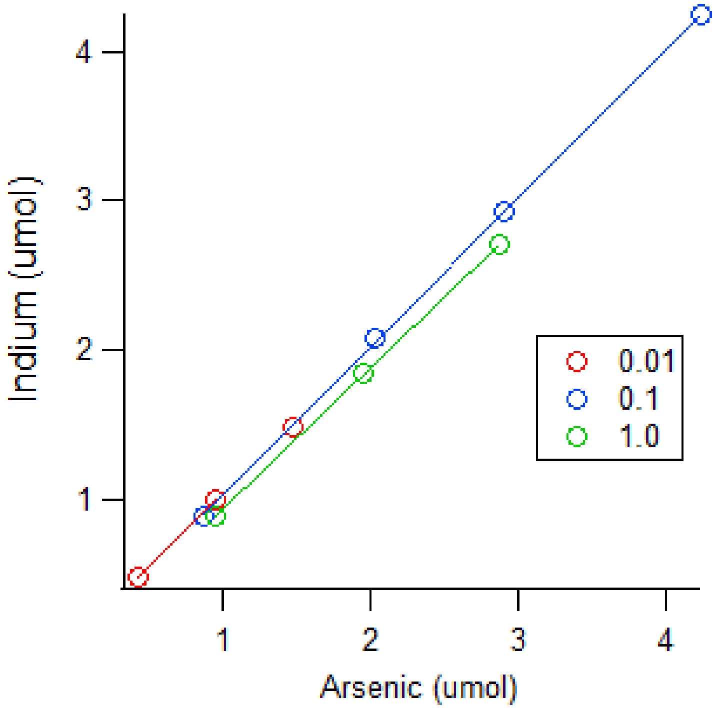
Total Mass Balance Experiment

- InAs (100)
  - 1x1 cm^2 samples patterned and unpatterned
- Etching rate
  - Unpatterned
    - Timed submersion in aqueous solutions.
      - [HCl]=0.01 M
      - [H_2O_2]=0.01, 0.1, 1.0 M.
    - No gas phase data.
    - ICP-MS analyzed samples for total masses of In and As
  - Patterned
    - Etch, remove photoresist, and measure amount etched by profilometry.

Total Mass Balance



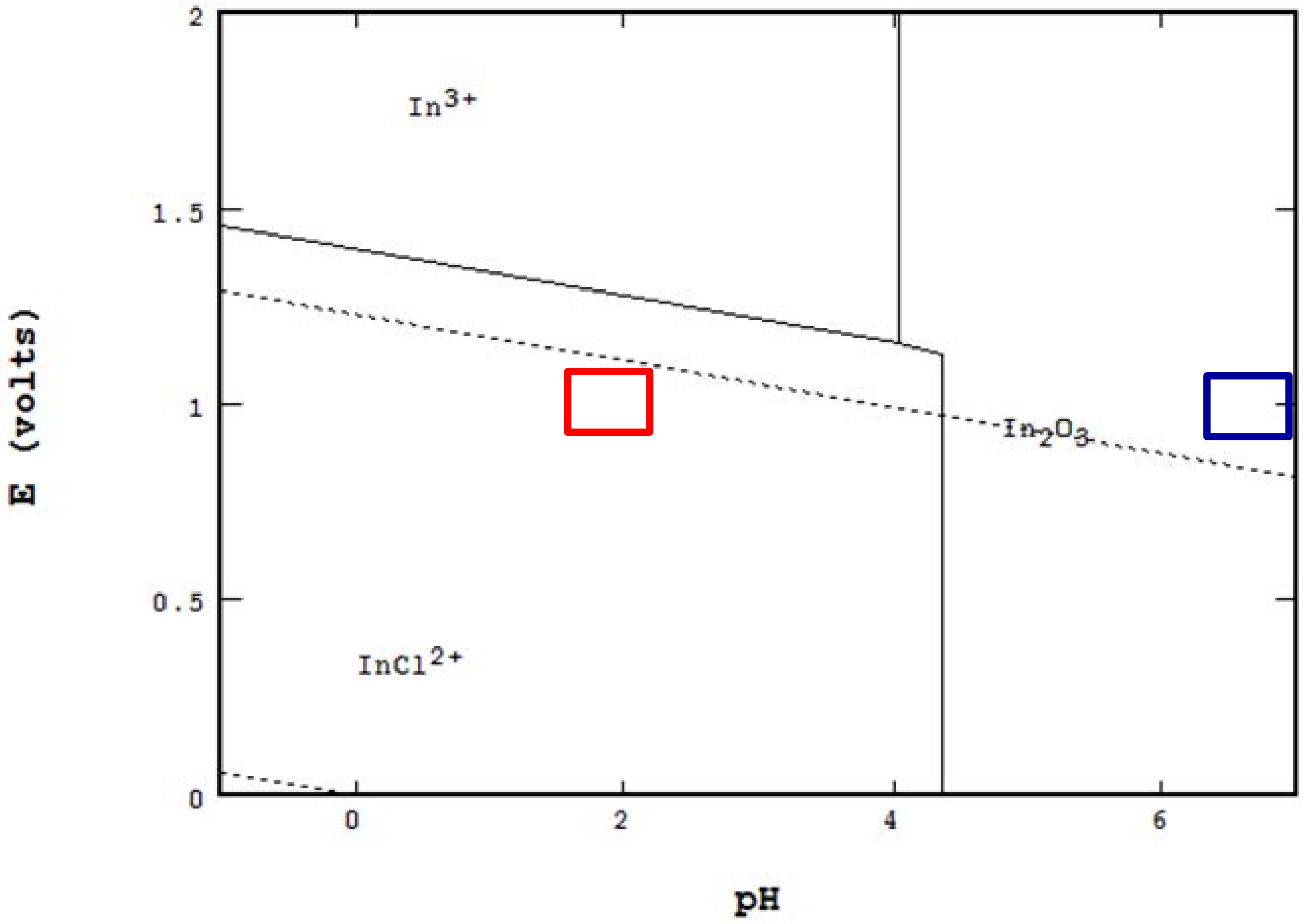
1:1 Ratio at Different [H_2O_2]



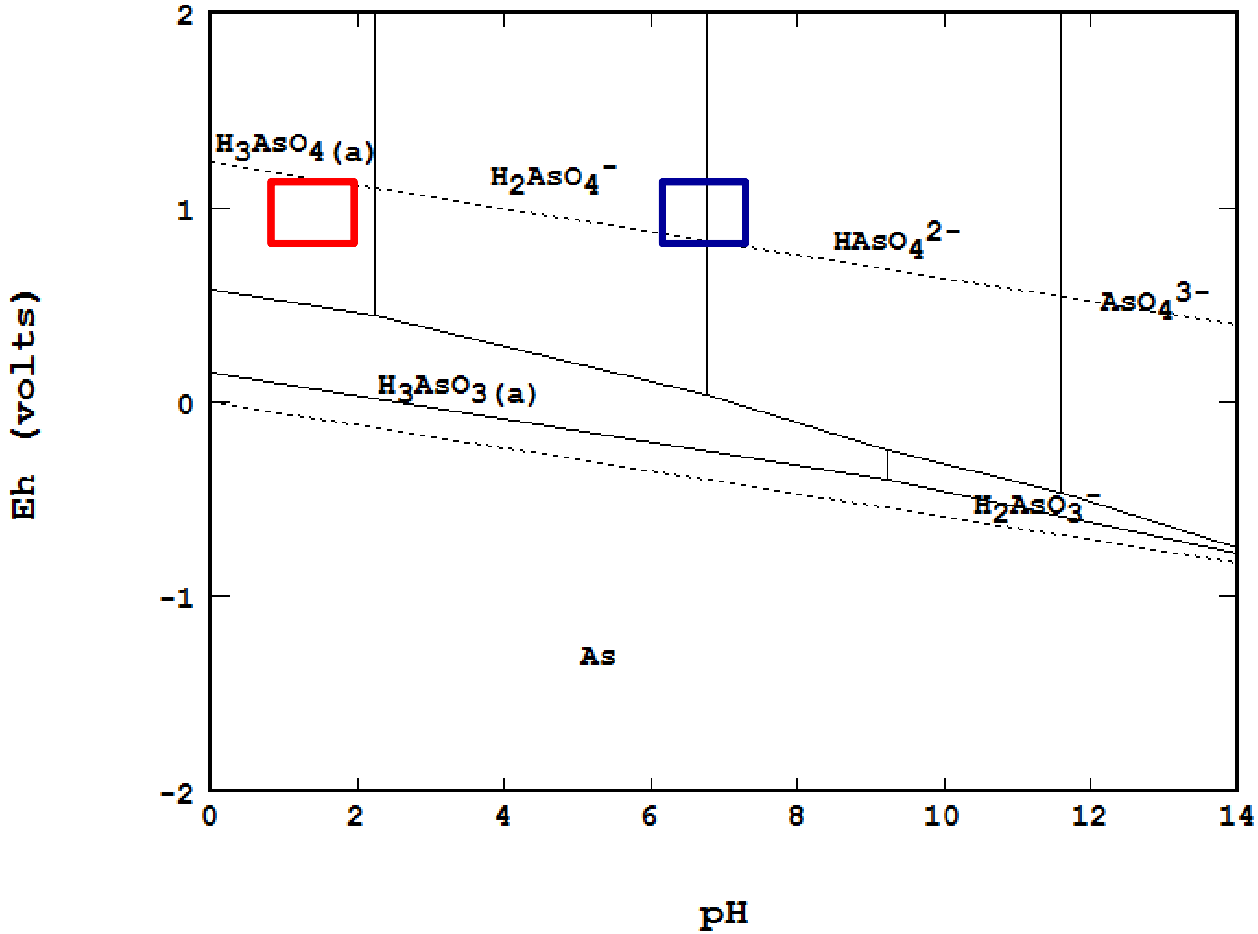
- **Species remain in liquid as predicted**

[H2O2]	Ratio
0.01	0.97 ± 0.04
0.1	0.99 ± 0.04
1.0	0.94 ± 0.03

In_2O_2 Expected at Neutral pH



Aqueous Arsenic Expected at Neutral pH



Conclusions

- **Aqueous species most 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 comparison of profilometry and ICP-MS etching rate data.**

- **In/As = 1:1 in solution suggests all species remain in liquid over range of interest for H_2O_2.**

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.**
  - **Perform neutralization experiment**

Industrial Interactions and Technology Transfer

Industrial liaisons:

Reed Content, Global EHS, Global Foundries, Santa Clara, CA

Brian Raley, Global EHS, Global Foundries, Austin, TX

David Speed, Microelectronics, IBM, Hopewell Junction, NY

Mansour Moinpour, Intel, Santa Clara, CA

Jim Powers, Intel, Portland, OR