Evaluation and Analysis of III-V ESH Processing Hazards

SESHA Hill Country Chapter
December 8, 2011

Brett Jay Davis, PE
Zephyr Environmental Corporation
I. Project Background
II. SVTC Process Engineers Mini-Survey Results
III. Texas State University Epi Process Tool Sample Set-Up and Analytical Results
IV. SVTC Process Tools Sample Set-Up and Analytical Results
V. Arsenic Wastewater Treatment Technologies
VI. Findings and Recommendations
VII. Future Work
VIII. Acknowledgements
IX. Questions?
I. Project Background
Compound (traditional Periodic Table Groups III-V) semiconductor films are being deposited on silicon dioxide wafers, at Texas State Univ. (TSU) in San Marcos, Texas, with further processing at SVTC in Austin, Texas.

Compound semiconductor processing utilizes a variety of III-V chemicals, such as arsenic, which have potentially unique ESH hazards.

Little work has been performed to understand the hazards posed by process materials, by-products, effluents and emissions from these processes.

To better understand the potential personnel and environmental exposures from III-V layering and processing, a detailed evaluation of processing operations was performed at TSU and SVTC, by Zephyr.
### Periodic Table of the Elements

**Lanthanide Series**

<table>
<thead>
<tr>
<th>Period</th>
<th>Symbol</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>La</td>
<td>138.9</td>
</tr>
<tr>
<td>7</td>
<td>Ce</td>
<td>140.1</td>
</tr>
<tr>
<td>8</td>
<td>Pr</td>
<td>140.9</td>
</tr>
<tr>
<td>9</td>
<td>Nd</td>
<td>144.2</td>
</tr>
<tr>
<td>10</td>
<td>Pm</td>
<td>145.0</td>
</tr>
<tr>
<td>11</td>
<td>Sm</td>
<td>150.4</td>
</tr>
<tr>
<td>12</td>
<td>Eu</td>
<td>152.0</td>
</tr>
<tr>
<td>13</td>
<td>Gd</td>
<td>157.2</td>
</tr>
<tr>
<td>14</td>
<td>Tb</td>
<td>158.9</td>
</tr>
<tr>
<td>15</td>
<td>Dy</td>
<td>162.5</td>
</tr>
<tr>
<td>16</td>
<td>Ho</td>
<td>164.9</td>
</tr>
<tr>
<td>17</td>
<td>Er</td>
<td>167.3</td>
</tr>
<tr>
<td>18</td>
<td>Tm</td>
<td>173.0</td>
</tr>
<tr>
<td>19</td>
<td>Yb</td>
<td>175.0</td>
</tr>
</tbody>
</table>

**Actinide Series**

<table>
<thead>
<tr>
<th>Period</th>
<th>Symbol</th>
<th>Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Ac</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>Th</td>
<td>232</td>
</tr>
<tr>
<td>8</td>
<td>Pa</td>
<td>231</td>
</tr>
<tr>
<td>9</td>
<td>U</td>
<td>238</td>
</tr>
<tr>
<td>10</td>
<td>Np</td>
<td>237</td>
</tr>
<tr>
<td>11</td>
<td>Pu</td>
<td>242</td>
</tr>
<tr>
<td>12</td>
<td>Am</td>
<td>243</td>
</tr>
<tr>
<td>13</td>
<td>Cm</td>
<td>247</td>
</tr>
<tr>
<td>14</td>
<td>Bk</td>
<td>247</td>
</tr>
<tr>
<td>15</td>
<td>Cf</td>
<td>251</td>
</tr>
<tr>
<td>16</td>
<td>Es</td>
<td>252</td>
</tr>
<tr>
<td>17</td>
<td>Fm</td>
<td>257</td>
</tr>
<tr>
<td>18</td>
<td>Md</td>
<td>258</td>
</tr>
<tr>
<td>19</td>
<td>No</td>
<td>259</td>
</tr>
<tr>
<td>20</td>
<td>Lr</td>
<td>262</td>
</tr>
</tbody>
</table>

**Period**

<table>
<thead>
<tr>
<th>Group</th>
<th>1A</th>
<th>2A</th>
<th>3A</th>
<th>4A</th>
<th>5A</th>
<th>6A</th>
<th>7A</th>
<th>8A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Li</td>
<td>Be</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Na</td>
<td>Mg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>K</td>
<td>Ca</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Rb</td>
<td>Sr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Cs</td>
<td>Ba</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Fr</td>
<td>Ra</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Group**

<table>
<thead>
<tr>
<th>Group</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>H</td>
<td>Li</td>
<td>Na</td>
<td>K</td>
<td>Rb</td>
<td>Cs</td>
<td>Fr</td>
<td>Ac</td>
</tr>
<tr>
<td>2A</td>
<td>He</td>
<td>Be</td>
<td>Mg</td>
<td>Ca</td>
<td>Sr</td>
<td>Ba</td>
<td>Ra</td>
<td>Th</td>
</tr>
<tr>
<td>3A</td>
<td>****</td>
<td>****</td>
<td>****</td>
<td>****</td>
<td>****</td>
<td>****</td>
<td>****</td>
<td>****</td>
</tr>
</tbody>
</table>

*Periodic Table of the Elements © 2023 Zephyr*
II. SVTC Process Engineers Mini-Survey Results
A. III-V Process Chemistries and By-Products

For the tools that you are familiar with, please complete the following table related to process chemicals and suspected by-products and residues, during III-V processing only, i.e., normal processing and invasive tasks (such as troubleshooting, daily PMs and major PMs, but not “end of life” tool, infrastructure and process issues).

This information is needed to identify unique III-V process chemicals used and by-products formed. The knowledge will inform the industrial hygiene and environmental sampling and analyses to be conducted for this project.

<table>
<thead>
<tr>
<th>Process Type</th>
<th>Tool ID</th>
<th>Process Chemicals</th>
<th>Suspected By-Products and Residues</th>
<th>Engineer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Etch-Dep</td>
<td>CVD08</td>
<td>NH3, NF3, CF4 N2O, C2F6, SiH4, PH3, N2, O3, He, O2, Ar, 3Ms (trimethyl silane)</td>
<td>Putting on layer of oxide/nitride. No concern</td>
<td>Sidi</td>
</tr>
<tr>
<td>Dry Etch – PVD</td>
<td>MTL06</td>
<td>N2, O2, Ar</td>
<td>Minimal: sputtering may dislodge As/Sb</td>
<td>Ed</td>
</tr>
<tr>
<td>Dry Etch</td>
<td>PET28BM</td>
<td>Cl2, HBr, CHF3, CF4 NF3, O2, He, O2, CO, BCL3, N2, Ar (red used by III-V)</td>
<td>As/Sb containing by product gas, pumped out by system; minutes in chamber</td>
<td>Gabe</td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTS07/8</td>
<td>HF, HCL, H2SO4, BOE, NH4OH</td>
<td>As/Sb particles in chemical waste</td>
<td>Mark</td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTS92</td>
<td>HF, HNO3</td>
<td>Back side clean, minimal waste</td>
<td>Ray</td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTC04</td>
<td>H2O2, NH4OH, HCL, H2SO4, HF</td>
<td>As/Sb particles in chemical waste</td>
<td>Mark</td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM1</td>
<td>Ar, O2, NH3, O3</td>
<td>Putting additional films. At high temp might be out-gassing As/Sb. Minutes to hours in chamber</td>
<td>Sidi</td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM2</td>
<td>Ar, O3</td>
<td>Depositing oxide/nitride. No concern</td>
<td>Sidi</td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM3</td>
<td>Ar, NH3, O3</td>
<td>Depositing oxide/nitride. No concern</td>
<td>Sidi</td>
</tr>
<tr>
<td>CMP</td>
<td>PLN93</td>
<td>H2O2, slurry, H2O</td>
<td>As, Sb on pads</td>
<td>Ed</td>
</tr>
<tr>
<td>Asher</td>
<td>ASH07</td>
<td>H2/N2, CF4, N2, O2</td>
<td>Affects resists, will be seeing some As/Sb</td>
<td>John</td>
</tr>
</tbody>
</table>
A. III-V Process Chemistries and By-Products (Continued)

**Potential Personnel Exposures**

For the tools that you are familiar with, please list the materials that workers might possibly be exposed to during normal processing or preventive maintenance, *during III-V processing and preventive maintenance after III-V processing*.

This information is needed to determine where industrial hygiene personnel sampling should be performed.

<table>
<thead>
<tr>
<th>Process Type</th>
<th>Tool ID</th>
<th>Clean Room Operator During Process</th>
<th>Equipment Technician During Preventive Maintenance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Etch – CVD</td>
<td>CVD08</td>
<td>As, Sb (only if a gas leak)</td>
<td>As, Sb dust, flaking, broken wafers</td>
</tr>
<tr>
<td>Dry Etch – PVD</td>
<td>MTL06</td>
<td>None expected</td>
<td>As, Sb dust, flaking, broken wafers</td>
</tr>
<tr>
<td>Dry Etch</td>
<td>PET28BM</td>
<td>As, Sb ? (Other reaction gas?)</td>
<td>As, Sb dust, flaking, broken wafers</td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTS97/8</td>
<td>None</td>
<td>Filter changes, broken lines</td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTS92</td>
<td>None</td>
<td>Filter changes, broken lines</td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTC04</td>
<td>None</td>
<td>Filter changes, broken lines</td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM1</td>
<td>As, Sb (only if a gas leak)</td>
<td>As, Sb dust, flaking, broken wafers</td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM2</td>
<td>As, Sb (only if a gas leak)</td>
<td>As, Sb dust, flaking, broken wafers</td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM3</td>
<td>As, Sb (only if a gas leak)</td>
<td>As, Sb dust, flaking, broken wafers</td>
</tr>
<tr>
<td>CMP</td>
<td>PLN93</td>
<td>During Pad change out</td>
<td>Contaminated pads, broken wafers</td>
</tr>
<tr>
<td>Asher</td>
<td>ASH07</td>
<td>As, Sb (only if a gas leak)</td>
<td>As, Sb dust, flaking, broken wafers</td>
</tr>
</tbody>
</table>

This information indicated that only As and AsH₃ are new to silicon manufacturing and with sufficient toxicity to merit IH-type sampling.
B. Likely Environmental Discharges

For the tools that you are familiar with, please complete the following table related to any materials discharged during III-V processing.

This information is needed to determine which materials need to be sampled and analyzed.

<table>
<thead>
<tr>
<th>Process Type</th>
<th>Tool ID</th>
<th>Wastewater (List Potential Materials or Indicate None)</th>
<th>Waste Wet Etch Acids (List Potential Materials or Indicate None)</th>
<th>Exhaust Air (List Potential Materials or Indicate None)</th>
<th>Chamber Surfaces (List Potential Materials or Indicate None)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Etch – CVD</td>
<td>CVD08</td>
<td>NONE</td>
<td>NONE</td>
<td>NONE</td>
<td>NONE</td>
</tr>
<tr>
<td>Dry Etch – PVD</td>
<td>MTL06</td>
<td>NONE</td>
<td>NONE</td>
<td>As, Sb</td>
<td>NONE</td>
</tr>
<tr>
<td>Dry Etch</td>
<td>PET28BM</td>
<td>NONE</td>
<td>NONE</td>
<td>As, Sb</td>
<td>NONE</td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTS07/8</td>
<td>As, Sb</td>
<td>HF, BOE (HF&amp;HCL)As, Sb</td>
<td>NONE</td>
<td>As, Sb</td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTS92</td>
<td>As, Sb</td>
<td>HF, HCL, H2SO4, BOE, NH4OH, As, Sb</td>
<td>NONE</td>
<td>NONE</td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTC04</td>
<td>As, Sb</td>
<td>H2O2, NH4OH, HCL, H2SO4, HF As, Sb</td>
<td>NONE</td>
<td>NONE</td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM1</td>
<td>NONE</td>
<td>NONE</td>
<td>As, Sb</td>
<td>NONE</td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM2</td>
<td>NONE</td>
<td>NONE</td>
<td>NONE</td>
<td>NONE</td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM3</td>
<td>NONE</td>
<td>NONE</td>
<td>NONE</td>
<td>NONE</td>
</tr>
<tr>
<td>CMP</td>
<td>PLN93</td>
<td>As, Sb, maybe</td>
<td>H2O2, As, Sb maybe</td>
<td>NONE</td>
<td>As, Pb</td>
</tr>
<tr>
<td>Asher</td>
<td>ASH07</td>
<td>NONE</td>
<td>NONE</td>
<td>As, Sb</td>
<td></td>
</tr>
</tbody>
</table>

This information indicated that only As and AsH₃ are new to silicon manufacturing and with sufficient toxicity to merit environmental sampling.
C. Opportunities for Sampling

For the tools that you are familiar with, please enter the projected timeframe of the next III-V processing and preventive maintenance activities, after III-V processing activity.

This information is needed to schedule industrial hygiene sampling.

<table>
<thead>
<tr>
<th>Process Type</th>
<th>Tool ID</th>
<th>Next III-V Processing</th>
<th>Next Preventive Maintenance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(Approximate Date(s))</td>
<td>(Approximate Date(s))</td>
</tr>
<tr>
<td>Dry Etch – CVD</td>
<td>CVD08</td>
<td>Once a month to once every 2 months</td>
<td></td>
</tr>
<tr>
<td>Dry Etch – PVD</td>
<td>MTL06</td>
<td>Once a week</td>
<td></td>
</tr>
<tr>
<td>Dry Etch</td>
<td>PET28BM</td>
<td>Never</td>
<td></td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTS07/8</td>
<td>Bath changes approx 1/week</td>
<td></td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTS92</td>
<td>Every Wednesday</td>
<td></td>
</tr>
<tr>
<td>Wet Etch</td>
<td>WTC04</td>
<td>Bath changes approx 1/week</td>
<td></td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM1</td>
<td>Rarely</td>
<td></td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM2</td>
<td>Rarely</td>
<td></td>
</tr>
<tr>
<td>Deposition – ALD</td>
<td>ALD02PM3</td>
<td>Rarely</td>
<td></td>
</tr>
<tr>
<td>CMP</td>
<td>PLN93</td>
<td>Toss pads weekly</td>
<td></td>
</tr>
<tr>
<td>Asher</td>
<td>ASH07</td>
<td>1/year</td>
<td></td>
</tr>
</tbody>
</table>

This information indicated that little maintenance sampling would be possible.
III. Texas State University Epi Process Tool Sample Set-Up and Analytical Results

Note: In all cases, for arsine air sampling, a modified NIOSH 6001 method, inclusive of a pre-filter, was used and for arsenic air sampling, a modified NIOSH 7300 method was used. For arsenic surface sampling, the NIOSH 9100 method was used.
Epi Tool at Texas State University

Back of tool showing pumps collecting from exhaust and near back of reactor

Exhaust Sample System

Sorbent tube for arsine – Note filter cassette pre-filter = Modified NIOSH 6001 Method

Close up of exhaust sample system

Filter cassette for arsenic = Modified NIOSH 7300 Method

Sampling pumps – High flow for arsenic, low flow for arsine
Epi Tool at Texas State University

Inside load lock - wipe collected from bottom

Load lock chamber lid – wipe collected from bottom
### Epi Tool Analytical Results

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>As Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBE/TSUEPI</td>
<td>Exhaust – Ion Pump</td>
<td>BDL / BDL</td>
<td>1554 / 1168</td>
<td>&lt;0.000097 / &lt;0.00013</td>
</tr>
<tr>
<td>MBE/TSUEPI</td>
<td>Above Load Lock</td>
<td>BDL / BDL</td>
<td>1717 / 1168</td>
<td>&lt;0.000087 / &lt;0.00013</td>
</tr>
<tr>
<td>MBE/TSUEPI</td>
<td>Back</td>
<td>BDL / BDL</td>
<td>1575 / 1239</td>
<td>&lt;0.000095 / &lt;0.00012</td>
</tr>
<tr>
<td>MBE/TSUEPI</td>
<td>Load Lock Lid Wipe</td>
<td>29 ug*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBE/TSUEPI</td>
<td>Bottom of Load Lock Wipe</td>
<td>120 ug*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>AsH₃ Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBE/TSUEPI</td>
<td>Exhaust – Ion Pump</td>
<td>BDL</td>
<td>102.7 / 11.5</td>
<td>&lt;0.0003 / &lt;0.003</td>
</tr>
<tr>
<td>MBE/TSUEPI</td>
<td>Above Load Lock</td>
<td>BDL</td>
<td>118.3 / 11.2</td>
<td>&lt;0.0003 / &lt;0.003</td>
</tr>
<tr>
<td>MBE/TSUEPI</td>
<td>Back</td>
<td>BDL</td>
<td>100.9 / 9.57</td>
<td>&lt;0.0003 / &lt;0.004</td>
</tr>
</tbody>
</table>

* Wipes are typically for 100 cm² of surface. Action level typically 50 ug.
  BDL <0.11 ug for Arsine and <0.15 ug for Arsenic in air samples
  BDL <1 ug for wipes
IV. SVTC Process Tools
Sample Set-Up and Analytical Results

Note: The asher and CMP tools were not included in the SVTC processing scheme and therefore were not sampled. Wastewater was not sampled as drain lines at SVTC did not have existing sampling ports. The wet etch tool WTS07/08 was replaced by the wet hood WTS91.
Pet28 Front samples
# Dry Etch Tool Analytical Results

## Dry Etch Tool Analytical Results Table

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>As Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Etch/PET28</td>
<td>Exhaust</td>
<td>BDL</td>
<td>Pump Fault</td>
<td>-</td>
</tr>
<tr>
<td>Dry Etch/PET28</td>
<td>Front</td>
<td>BDL</td>
<td>116</td>
<td>&lt;0.0013</td>
</tr>
<tr>
<td>Dry Etch/PET28</td>
<td>Back</td>
<td>BDL</td>
<td>120</td>
<td>&lt;0.0013</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>AsH₃ Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Etch/PET28</td>
<td>Exhaust</td>
<td>BDL</td>
<td>8.21</td>
<td>&lt;0.004</td>
</tr>
<tr>
<td>Dry Etch/PET28</td>
<td>Front</td>
<td>BDL</td>
<td>8.16</td>
<td>&lt;0.004</td>
</tr>
<tr>
<td>Dry Etch/PET28</td>
<td>Back</td>
<td>BDL</td>
<td>6.77</td>
<td>&lt;0.005</td>
</tr>
</tbody>
</table>

BDL <0.11 ug for Arsine and <0.15 ug for Arsenic
First Wet Etch Tool at SVTC

WTS92 Front
First Wet Etch Tool Analytical Results

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>As Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Etch/WTS92</td>
<td>Front</td>
<td>BDL</td>
<td>48.3</td>
<td>&lt;0.0031</td>
</tr>
<tr>
<td>Wet Etch/WTS92</td>
<td>Back</td>
<td>BDL</td>
<td>50.55</td>
<td>&lt;0.0030</td>
</tr>
<tr>
<td>Wet Etch/WTS92</td>
<td>Exhaust</td>
<td>BDL</td>
<td>56.64</td>
<td>&lt;0.0026</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>AsH₃ Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Etch/WTS92</td>
<td>Front</td>
<td>BDL</td>
<td>3.19</td>
<td>&lt;0.011</td>
</tr>
<tr>
<td>Wet Etch/WTS92</td>
<td>Back</td>
<td>BDL</td>
<td>3.41</td>
<td>&lt;0.010</td>
</tr>
<tr>
<td>Wet Etch/WTS92</td>
<td>Exhaust</td>
<td>BDL</td>
<td>3.42</td>
<td>&lt;0.010</td>
</tr>
</tbody>
</table>

BDL <0.11 ug for Arsine and <0.15 ug for Arsenic
Wet Clean Tool at SVTC

WTC04 Front Sample System

Chemicals in use: hydrochloric acid, ammonium hydroxide
### Wet Clean Tool Analytical Results

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>As Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Etch/WTC04</td>
<td>Exhaust</td>
<td>BDL</td>
<td>287</td>
<td>&lt;0.00052</td>
</tr>
<tr>
<td>Wet Etch/WTC04</td>
<td>Front</td>
<td>BDL</td>
<td>273.1</td>
<td>&lt;0.00055</td>
</tr>
<tr>
<td>Wet Etch/WTC04</td>
<td>Back</td>
<td>BDL</td>
<td>289.5</td>
<td>&lt;0.00052</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>AsH₃ Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Etch/WTC04</td>
<td>Exhaust</td>
<td>BDL</td>
<td>36.08</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Wet Etch/WTC04</td>
<td>Front</td>
<td>BDL</td>
<td>12.14</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td>Wet Etch/WTC04</td>
<td>Back</td>
<td>BDL</td>
<td>18.7</td>
<td>&lt;0.002</td>
</tr>
</tbody>
</table>

BDL <0.11 ug for Arsine and <0.15 ug for Arsenic
Deposition Tool at SVTC

ALD02 Exhaust Sample System 2

Chemicals in use: ozone, trimethyl aluminum and argon

ALD02 Front Sample System
Deposition Tool at SVTC

ALD02 Exhaust Sample System

ALD02 Back Sample System
Deposition Tool Analytical Results

BDL <0.11 ug for Arsine and <0.15 ug for Arsenic
Chemical Vapor Deposition Tool at SVTC

CVD08 Front Sample System

Chemicals in use: TEOS and oxygen
**Chemical Vapor Deposition Tool at SVTC**

### Arsine Results

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>As Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Etch/CVD08</td>
<td>Exhaust</td>
<td>BDL</td>
<td>295.68</td>
<td>&lt;0.00051</td>
</tr>
<tr>
<td>Dry Etch/CVD08</td>
<td>Front</td>
<td>BDL</td>
<td>273.06</td>
<td>&lt;0.00055</td>
</tr>
<tr>
<td>Dry Etch/CVD08</td>
<td>Back</td>
<td>BDL</td>
<td>285.6</td>
<td>&lt;0.00053</td>
</tr>
</tbody>
</table>

### Arsenic Results

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>AsH₃ Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Etch/CVD08</td>
<td>Exhaust</td>
<td>BDL</td>
<td>12.516</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td>Dry Etch/CVD08</td>
<td>Front</td>
<td>BDL</td>
<td>20.172</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Dry Etch/CVD08</td>
<td>Back</td>
<td>BDL</td>
<td>17.556</td>
<td>&lt;0.002</td>
</tr>
</tbody>
</table>

BDL <0.11 ug for Arsine and <0.15 ug for Arsenic
Second Wet Etch Tool at SVTC

WTS91 Front

WTS91 Spin Rise Dryer Sample System

Chemicals in use: dilute phosphoric acid and hydrogen peroxide
## Second Wet Etch Tool Analytical Results

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>As Results</th>
<th>Sample Volume (L)</th>
<th>Concentration (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Etch/WTS91</td>
<td>Exhaust</td>
<td>BDL</td>
<td>287</td>
<td>&lt;0.00052</td>
</tr>
<tr>
<td>Wet Etch/WTS91</td>
<td>Front</td>
<td>BDL</td>
<td>273.1</td>
<td>&lt;0.00055</td>
</tr>
<tr>
<td>Wet Etch/WTS91</td>
<td>Back</td>
<td>BDL</td>
<td>289.5</td>
<td>&lt;0.00052</td>
</tr>
<tr>
<td>Wet Etch/WTS91</td>
<td>Acid Bath</td>
<td>BDL</td>
<td></td>
<td>See Note</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>AsH₃ Results</th>
<th>Sample Volume (L)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet Etch/WTS91</td>
<td>Exhaust</td>
<td>BDL</td>
<td>36.08</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Wet Etch/WTS91</td>
<td>Front</td>
<td>BDL</td>
<td>12.14</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td>Wet Etch/WTS91</td>
<td>Back</td>
<td>BDL</td>
<td>18.7</td>
<td>&lt;0.002</td>
</tr>
</tbody>
</table>

BDL <0.11 ug for Arsine and < 0.15 ug for Arsenic (in air) and <1 mg/Kg (in liquid)
Metal sources in use: molybdenum, ruthenium, tungsten, hafnium
Metal Deposition Tool at SVTC

MTL06 Open Maintenance Sample System

MTL06 Target Maintenance Sample System
Metal Deposition Tool at SVTC

MTL06 Wafer Stand Wipe

MTL06 Target Perimeter Wipe

Chemicals in use: argon and nitrogen
**Metal Deposition Tool Analytical Results**

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>As Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Etch/MTL06</td>
<td>Front</td>
<td>BDL</td>
<td>201</td>
<td>&lt;0.000075</td>
</tr>
<tr>
<td>Dry Etch/MTL06</td>
<td>Back</td>
<td>BDL</td>
<td>205.6</td>
<td>&lt;0.000073</td>
</tr>
<tr>
<td>Dry Etch/MTL06</td>
<td>Maintenance</td>
<td>BDL</td>
<td>156.04</td>
<td>&lt;0.000096</td>
</tr>
<tr>
<td>Dry Etch/MTL06</td>
<td>Stand Wipe</td>
<td>BDL*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry Etch/MTL06</td>
<td>Target Wipe</td>
<td>BDL*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process/Tool ID</th>
<th>Sample Location</th>
<th>AsH₃ Results</th>
<th>Sample Volume (l)</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Etch/MTL06</td>
<td>Front</td>
<td>BDL</td>
<td>13.73</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td>Dry Etch/MTL06</td>
<td>Back</td>
<td>BDL</td>
<td>12.12</td>
<td>&lt;0.003</td>
</tr>
<tr>
<td>Dry Etch/MTL06</td>
<td>Maintenance</td>
<td>BDL</td>
<td>14.805</td>
<td>&lt;0.002</td>
</tr>
</tbody>
</table>

BDL <0.11 ug for Arsine and < 0.15 ug for Arsenic for air samples
BDL <1 ug for wipes
Sampling Results Summary

• Except for the MBE tool load lock, no arsenic or arsine was detected at above analytical detection method limits.
  – Note: Due to the short process and sampling durations, this information cannot be correlated with personnel exposure limits, which are typically defined as average exposures over eight-hours.
    • ACGIH TLV-TWA = 0.005 ppm ASH$_3$
    • ACGIH TLV-TWA = 0.01 mg/m$^3$ As
V. Arsenic Wastewater Treatment Technologies
In early 2011, Zephyr was retained by ISMI to perform an assessment of available arsenic removal technologies.

The purpose of the project was to provide guidance on the possible treatment of arsenic from the application and processing of compound (III-V) semiconductor films on silicon oxide substrates, as presently being demonstrated at SVTC in Austin, Texas.

The resulting table of available technologies and their capabilities and limitations follows.
<table>
<thead>
<tr>
<th>Treatment Technology Category</th>
<th>Specific Treatment Technology</th>
<th>As Removal Efficiency (%)</th>
<th>Pre-Treatment Requirements</th>
<th>Wastes Generated</th>
<th>Upper As Limit (mg/L)</th>
<th>Lower Treatment Limits (mg/L)</th>
<th>Limitations</th>
<th>Advantages</th>
<th>Relative Operator Skill</th>
<th>Relative Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption Processes</td>
<td>Anionic Exchange (IX)</td>
<td>95-99</td>
<td>Pre-filter (Remove particulate, TOC), Pre-Oxidize to As(V)</td>
<td>Spent resin, spent regeneration brine (backwash may be hazardous)</td>
<td>0.003 - 0.002</td>
<td>Potentially acidic discharge, other constituents in water can compete with resin sites (e.g., sulfate), sharp As breakthrough, large amount of salt required</td>
<td>Empty bed contact time (EBCT) of 1.5 min, unaffected by pH (5 – 9), easily automated</td>
<td>High</td>
<td>High</td>
<td></td>
</tr>
<tr>
<td>Hybrid Iron-impregnated IX</td>
<td>Remove particulate, Pre-Oxidize to As(V)</td>
<td></td>
<td></td>
<td>Spent resin, spent regeneration brine (backwash may be hazardous)</td>
<td>0.004 - 0.002</td>
<td>Arsenic breakthrough is gradual, resulting in unutilized capacity; affected by sulfate (not removed during regeneration), phosphate and vanadium</td>
<td>Not affected by sulfate, longer runs than IX</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated Alumina (AAl) Sorbents</td>
<td>Remove particulate, Pre-Oxidize to As(V)</td>
<td>90 – 95</td>
<td>Spent media (non-regenerable – may not be hazardous waste per TCLP)</td>
<td>0.16</td>
<td>0.003</td>
<td>Slow kinetics, 5 – 12 min. EBCT, inconsistent results, operating pH 5.5-6.5, silicate, phosphate, and vanadium compete for adsorption sites</td>
<td>Low-cost media</td>
<td>Low</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Iron-doped Activated Alumina</td>
<td>Remove particulate, Pre-Oxidize to As(V)</td>
<td>90 – 95</td>
<td>Spent media (non-regenerable)</td>
<td>0.003</td>
<td>Slow kinetics, 5 – 12 min. EBCT, inconsistent results</td>
<td>Operating pH up to 7.5, may be non-RCRA HW</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iron Based Sorbents</td>
<td>Remove particulate (iron, manganese) and TOC, Pre-Oxidize to As(V)</td>
<td>98</td>
<td>Spent resin, spent regeneration brine (backwash may be hazardous)</td>
<td>0.003</td>
<td>Silicate, phosphate, or vanadium, can reduce effectiveness, 3 – 6 min. EBCT</td>
<td>Operates at higher pH than AAI, not affected by sulfate</td>
<td>Low</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treatment Technology Category</td>
<td>Specific Treatment Technology</td>
<td>As Removal Efficiency (%)</td>
<td>Pre-Treatment Requirements</td>
<td>Wastes Generated</td>
<td>Upper As Limit (mg/L)</td>
<td>Lower Treatment Limits (mg/L)</td>
<td>Limitations</td>
<td>Advantages</td>
<td>Relative Operator Skill</td>
<td>Relative Cost</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>--------------------------------</td>
<td>---------------------------</td>
<td>---------------------------</td>
<td>------------------</td>
<td>----------------------</td>
<td>-----------------------------</td>
<td>----------------</td>
<td>----------------</td>
<td>------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Titanium- or Zirconium-oxide–based media</td>
<td>Remove particulate, Pre-Oxidize to As(V)</td>
<td>90 (for canisters in series)</td>
<td>Pre-oxidation not required</td>
<td>Spent media (non-regenerable – may not be hazardous waste per TCLP)</td>
<td>&lt;0.020 to 0.002</td>
<td>3 to 6 min EBCT, Phosphate can compete for adsorption sites</td>
<td>Phosphate, silica, and vanadate can reduce effectiveness, Ti and Zr not as effective as FeCl₃ at pH 6.5 and 7.5.</td>
<td>At pH 8.5, TiCl₃ equiv to FeCl₃, For As(III), TiCl₃ is best at pH 6.5 and 7.5.</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Granular Ferric Hydroxide</td>
<td>95</td>
<td>Pre-Oxidize to As(V)</td>
<td>Sludge (must be dewatered prior to disposal – may be non-hazardous waste)</td>
<td>None</td>
<td>0.005-0.002</td>
<td>5 to 100 psi, Phosphate and silica can reduce effectiveness, lower treatment pH better, membrane fouled by organic carbon, requires compressed air for backwashing, lower pH discharge requires pH adjustment, retentate sludge must be dewatered prior to disposal</td>
<td>Good for small systems, consistent results</td>
<td>High</td>
<td>Medium</td>
<td></td>
</tr>
<tr>
<td>Precipitation/ Co-Precipitation</td>
<td>Ferric Coagulation and Microfiltration</td>
<td>95</td>
<td>Pre-Oxidize to As(V)</td>
<td>Backwash sludge (must be dewatered prior to disposal – may be non-hazardous waste)</td>
<td>None</td>
<td>0.005-0.002</td>
<td>Phosphate and silica can reduce effectiveness, results highly dependent on filtration capture.</td>
<td>Good for small systems, unaffected by organics</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>
### Arsenic Contaminated Wastewater Treatment Technologies (continued)

<table>
<thead>
<tr>
<th>Treatment Technology Category</th>
<th>Specific Treatment Technology</th>
<th>As Removal Efficiency (%)</th>
<th>Pre-Treatment Requirements</th>
<th>Wastes Generated</th>
<th>Upper As Limit (mg/L)</th>
<th>Lower Treatment Limits (mg/L)</th>
<th>Limitations</th>
<th>Advantages</th>
<th>Relative Operator Skill</th>
<th>Relative Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modified lime softening and clarification and filtration, pH adjustment</td>
<td>90</td>
<td>Pre-Oxidize to As(V)</td>
<td>Sludge</td>
<td>0.08</td>
<td>Operates best at pH &gt; 10.5</td>
<td>Good for influent conc. Of 50 ug/l</td>
<td>High</td>
<td>High</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressured Membrane Filtration</td>
<td>Nanofiltration</td>
<td>90-95</td>
<td>Pre-Oxidize to As(V), Remove organics and suspended solids, Possible pH adjustment</td>
<td>Reject water</td>
<td>50 to 150+ psi, MW 150+, Low permeate % may result in retentate treatment</td>
<td>Membranes don't retain As, Tests show can remove As(III) well, Combination with adsorption systems best for industrial applications</td>
<td>High</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>&gt;95</td>
<td>Pre-Oxidize to As(V), Remove organics and suspended solids, Possible pH adjustment</td>
<td>Reject water</td>
<td>0.16</td>
<td>&lt;0.01</td>
<td>Iron or manganese requires pre-treatment, 50 to 150+ psi, MW 1+, Low permeate % may result in retentate treatment</td>
<td>Membranes don't retain As, Combination with adsorption systems best for industrial applications</td>
<td>High</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystallization</td>
<td>Fluidized Bed Crystallization</td>
<td>Requires sulfide injection and low pH.</td>
<td>Crystals (can be dewatered and reused)</td>
<td>Reported to 0.5 mg/l levels</td>
<td>May not be able to treat to ug/l levels</td>
<td>Produces crystals thus reducing waste sludge by 75%</td>
<td>High</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Ion exchange is regenerable. Other sorbents are typically disposable.
2. For "enhanced" removal efficiency, iron hydroxide, instead of iron chloride, is used for coagulation and co-precipitation.
3. Electrical potential driven membrane processes, such as electrodialysis reversal (EDR), have also proven effective. IBM has been researching a new membrane that works well at high pH, by becoming charged and repelling charged As molecules. (See [http://beacon.trbot.com/biomedicine/22729/?a=f](http://beacon.trbot.com/biomedicine/22729/?a=f) for details.)
VI. Findings and Recommendations
As expected:

- Dry semiconductor processing of silicon wafers with gallium arsenide films, *did not* liberate arsenic or arsine into the workspace (at least not above detection limits).

- Wet semiconductor processing of silicon wafers with gallium arsenide films, *did not* liberate arsenic or arsine into the workspace or into an acid bath (at least not above detection limits).

This project did not detect EHS hazards that would require additional personnel protection or environmental controls, however:

- It is advisable to perform personnel monitoring for III-V processing at a production facility, preferably with lower method detection limits than those available for this project.
VII. Possible Future Work
Future Work

• Investigate ability to obtain lower detection limits – Portable FTIR?
• Perform wipe sample on load lock before and after processing
• Sample for off-gassing from wafer box
• Sample during maintenance of all wet and dry tools
• Sample wastewater discharged from wet etch and CMP processing
• Sample metal deposition tool exhaust
• Analyze waste wafers for TCLP concentrations
• Investigate need to repeat project for other Group V semiconductor compounds, such as antimony and bismuth
VIII. Acknowledgements
Acknowledgements

This project was successful thanks to the following people:

• The Banker – Steve Trammell, ISMI
• The Architects – Niti Goel, Wei-E Wang and Kevin Wolfe, Intel
• The Superintendent – Bob Bianconi, SVTC
• The Foremen – Barry Sassman and Melvin Cruz, ISMI
• The Builders – Tiffany Giles and Jeanne Yturri, Zephyr
• The Inspectors – Sara Brenner and Hallie Morgan, CNSE, and Galson Laboratories
IX. Questions?
Thank you!

Brett Jay Davis, PE
Zephyr Environmental Corporation
bdavis@zephyrenv.com
Phone: 512-879-6628