REAL TIME CONTROL OF ARSINE AND PHOSPHINE PURIFICATION PROCESS USING TDLS

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Introduction

High-purity AsH$_3$ and PH$_3$ are used for semiconductors production (GaAs, GaP, AlAs, InAs).
Quality of semiconductors manufactured depends on impurities presence. For required current carrier concentration below $10^{15}$ cm$^{-3}$, impurity concentration in hydrides has to be below 10 ppb. There are many possible impurities in hydrides. H$_2$O, NH$_3$, H$_2$S, CO$_2$, and C$_2$H$_4$ are considered as most important. In present paper we’ll present result for ammonia.
Goal: investigate possibility to use TDLS for real time ammonia concentration measurement in phosphine and arsine during their syntheses and purification.
High-purity arsine and phosphine production stages

There are 3 steps of high purity AsH$_3$ and PH$_3$ production:

1. Syntheses
   Phosphine
   $\text{Mg}_3\text{P}_2 + 6\text{HCl} \rightarrow 2\text{PH}_3 + 3\text{MgCl}_2$

   Arsine
   $\text{Mg}_3\text{As}_2 + 6\text{HCl} \rightarrow 2\text{AsH}_3 + 3\text{MgCl}_2$
   $\text{AsCl}_3 + 3\text{NaBH}_4 + 9\text{H}_2\text{O} \rightarrow \text{AsH}_3 + 3\text{NaCl} + 3\text{H}_3\text{BO}_3 + 9\text{H}_2$

2. Cryo-filtration
3. Rectification

Two last steps are subject for TDLS complexes application.
Rectification column

Block scheme and view of rectification column.

TDLS instrument measured NH$_3$ concentration in raw material or heavy fraction (HF) (green), pure (red), and light fraction (LF) (white) points of rectification column.
## Impurities in \( \text{AsH}_3 \) and \( \text{PH}_3 \)

<table>
<thead>
<tr>
<th>Controlled impurities</th>
<th>Impurity content, ppb</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Arsine</td>
<td>Phosphine</td>
</tr>
<tr>
<td></td>
<td>99,99994% Solkatronic Chemicals</td>
<td>99,9999% Solkatronic Chemicals</td>
</tr>
<tr>
<td>( \text{N}_2, \text{Ar, O}_2 )</td>
<td>&lt;50</td>
<td>&lt;100</td>
</tr>
<tr>
<td>( \text{CO, CO}_2 )</td>
<td>&lt;50</td>
<td>&lt;100</td>
</tr>
<tr>
<td>( \text{CH}_4, \text{C}_2\text{H}_6; \text{C}_3\text{H}_8 )</td>
<td>&lt;50</td>
<td>&lt;100</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4, \text{C}_3\text{H}_6 )</td>
<td>–</td>
<td>&lt;70,&lt;100</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>&lt;100</td>
<td>&lt;1000</td>
</tr>
<tr>
<td>( \text{GeH}_4, \text{SiH}_4 )</td>
<td>&lt;50, &lt;100</td>
<td>–</td>
</tr>
<tr>
<td>( \text{PH}_3 )</td>
<td>&lt;50</td>
<td>&lt;200</td>
</tr>
<tr>
<td>( \text{AsH}_3 )</td>
<td>–</td>
<td>&lt;100</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>&lt;50</td>
<td>&lt;200</td>
</tr>
</tbody>
</table>
TDLS complexes developed had similar module structure.

Arrows: blue – digital connection, red – analog signals, black – optical fibers.
TDLS complex view

Three cannels TDLS complex to detect ammonia in arsine and phosphine view.

Analytical cells

L=70, 140 cm

L=3, 5 cm
TDLS complex

All TDLS complexes contain the same set of components

National Instrument USB DAQ

Electronics developed by GPI and Canberra Albuquerque and manufactured by Canberra Albuquerque

View of reference channel
No significant AsH$_3$ and PH$_3$ absorption was observed in this spectral range.
Analytical signal

NH$_3$ line correlation functions in 4 channels: reference (yellow); raw (green), LF (white), pure (red).
Vapor above solution (Raoult law)

NH₃ concentration in gas phase as function of its concentration in liquid phase as measured by TDLS in arsine. Red – Raoult law (concentrations are equal).

Raul law is not valid for NH₃ in hydrides.
One more law is not valid

Traditional approach: Impurities having lower or higher vapor pressure than main molecule will concentrated in HF and LF, respectively.

$NH_3$ has lower vapor saturated pressure than $AsH_3$ and $PH_3$ and due to traditional approach has to be concentrated in HF.

Time dependence of $HN_3$ concentration as measured in three TDLS channels.

$NH_3$ in $AsH_3$ and $PH_3$ is concentrated in light fraction
System operation

Time dependence of NH$_3$ concentrations in three points of rectification column: raw (green), LF (white), pure (red).

End of purification can be easily identified
Additional diagnostics

Rectification columns have additional diagnostics: FTS, gas chromatography, and dew point temperature measurement.

FTS spectra at different moments of rectification process.

Presence of different impurities can be observed.

Intercomparison results of different diagnostic techniques of NH$_3$ detection: TDLS is 1-2 orders more sensitive than FTS and gas chromatography, is more operative in time scale, and can detect impurity in different points of rectification column. FTS and gas chromatography can detect simultaneously several impurities and give TDLS information of impurities to be detected.
Simultaneous analysis of LF content during arsine rectification process using FTS (upper) and TDLS (lower - ammonia concentration). For ammonia both techniques show similar behavior. Due to FTS results it was found that some impurities are removed from main purified material very quickly, some remained in it – subject for future TDLS development.
Conclusion

1. TDLS based complexes were developed to measure NH\textsubscript{3} in hydrides (see A3).
2. NH\textsubscript{3} was detected in raw samples of AsH\textsubscript{3} и PH\textsubscript{3}.
3. It was discovered that Raul law is invalid for NH\textsubscript{3} in hydrides.
4. It was discovered that traditional approach can not explain NH\textsubscript{3} behavior during AsH\textsubscript{3}, PH\textsubscript{3} и GeH\textsubscript{4} rectification.
5. TDLS technique was developed to control NH\textsubscript{3} behavior during AsH\textsubscript{3} and PH\textsubscript{3} rectification.
6. Technique developed was compared with FTS and gas chromatography. TDLS is 1-2 orders more sensitive than FTS and gas chromatography, is more operative in time scale, and can detect impurity in different points of rectification column. FTS and gas chromatography can detect simultaneously several impurities and give TDLS information of impurities to be detected.