Monitoring and control of binary gas mixtures from solid phase MOCVD sources using an acoustic sensor

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Issues with delivery of solid MOCVD precursors

- **Solid MOCVD sources used in compound semiconductors**
  - e.g. TMI in III/V GaN devices, Cp₂Mg for p doping
- **Dosimetry issues from use of MO solid sources**
  - Low vapor pressure: TMI (1.75 Torr), Cp₂Mg (0.05 Torr) at 25°C
  - Require heated source and feed lines
  - Instability of metal-organic feed rate due to:
    - Aging effects (change of crystal surface area, material redistribution, contamination) ⇒ Vapor Pressure variation
    - Interaction feed line / MO vapor ⇒ condensation
    - Incomplete saturation at high flows

- Reproducibility issues affect device performance
- Only small fraction of the source is used before being replaced

⇒ Need for real-time monitoring and control of the MO precursor concentration
Inficon “Composer”
acoustic transducer

Measurement of resonant frequency $F$

$$F = \frac{C}{2L} \quad \text{with} \quad C = \sqrt{\frac{\gamma_{\text{avg}} \, RT}{M_{\text{avg}}}}$$

- $C$: speed of sound, $L$: chamber length
- $T$: gas temperature
- $\gamma_{\text{avg}}$: average specific heat ratio
- $M_{\text{avg}}$: average molecular weight

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mol. weight (g/mol)</th>
<th>Res. Freq. (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>2</td>
<td>4000</td>
</tr>
<tr>
<td>$Cp_2Mg$</td>
<td>154.5</td>
<td>440</td>
</tr>
</tbody>
</table>

- If binary gas mixture (precursor, carrier)
- If $F_2$, carrier gas resonant frequency, is known
  $\Rightarrow F/F_2 = f$ (Precursor Mole Fraction)
- High mass ratio $\Rightarrow$ high sensitivity
Solid source gas delivery

Carrier gas (H₂) flown into temperature controlled sublimator to be saturated by source vapor pressure

Heated lines

H₂ carrier gas

H₂ dilution

MFC

H₂

50 g. MOCVD solid source

Pressure control valve

acoustic transducer

Temperature controlled bath (± 0.1°C)

Recommended temperatures

<table>
<thead>
<tr>
<th>Gas</th>
<th>Bath T (°C)</th>
<th>VP (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMI</td>
<td>25</td>
<td>2.54</td>
</tr>
<tr>
<td>Cp₂Mg</td>
<td>40</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Monitoring of TMI and Cp₂Mg concentration by acoustic sensing
Effect of pressure variations

- P > 150 Torr, composition measurements vary accordingly with VP / P
- At P < 50 Torr, measurement failure due to insufficient transfer of acoustic energy
- Between 50 and 150 Torr, higher concentration achievable but sensor response becomes non-linear vs. 1/P

➢ Varying pressure is not recommended to adjust composition due to effects of pressure change on acoustic measurements

H₂ carrier = 100 sccm
P varied from 500 to 50 Torr

Slope = 2.2 E-2,
VP = 2.44 Torr

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Ideal operating environment

- **Requirements in reactor**
  - Tune and maintain:
    - constant MO precursor concentration
    - constant gas throughput (H₂ carrier + dilution) to reactor

- **Requirements in delivery system**
  - Fixed pressure to minimize acoustic sensor drift (and potential failure at low pressure, < 50 Torr)
  - Controllable precursor concentration to compensate for change in source vapor pressure (temperature or aging effects)
Effect of H\textsubscript{2} flow rates

MO composition can not be reproducibly adjusted by varying carrier gas flow

- \( \sum (\text{carrier} + \text{dilution}) = \text{constant throughput} \)
- Composition adjusted by varying H\textsubscript{2} dilution flow rate

H\textsubscript{2} carrier flow / H\textsubscript{2} dilution flow (sccm)

P = 300 Torr

3E-5 mol\% Standard Deviation

\( \text{Cp}_2\text{Mg composition (mol \%)} \)

100/0 80/0 60/0 40/0 20/0 100/0

80/20 60/40 40/60 20/80 20/0
Can detect variation of \( \text{Cp}_2\text{Mg} \) concentration in \( \text{H}_2 \) of less than 1 ppm (based on 3E-5 mol % STD)

Can tune \( \text{Cp}_2\text{Mg} \) concentration by adjusting dilution flow

- 0.1 sccm change in \( \text{H}_2 \) dilution flow results in 5E-5 mol % composition change (at 100 sccm total flow)

Excellent prognosis for real-time control of MO feed rate
Effect of temperature drift in open loop configuration

- \(\text{Cp}_2\text{Mg} \) bath temperature varied from 40\(^\circ\)C to 32\(^\circ\)C
  - Vapor pressure down from 0.16 to 0.08 Torr
  - “Simulates” aging effects

- Open loop configuration:
  - Dilution flow = 100 sccm
  - Sublimator flow = 50 sccm
  - \(\text{Cp}_2\text{Mg} \) composition down from 0.01 to 0.005 mol%
Closed loop concentration control

H₂ dilution and carrier flows adjusted dynamically to keep composition on target
- Proportional Integral Derivative closed loop control
- Primary control variables adjusted every second
Effect of temperature drift on composition in closed loop control

- Source temperature varied from 40 to 32°C
- $\Sigma$ (H$_2$ flows) = 150 sccm, P = 300 Torr
- Cp$_2$Mg composition target = 0.01 mol% (0.3 umol/min)
Closed loop control performance

(Cp2Mg)average = 0.010009 mol %
(Cp2Mg) STD = 3.0 E-5 mol %

Cp2Mg composition controlled within a 1 % range despite variation of the source vapor pressure from 0.16 to 0.08 Torr.
Closed loop control in presence of short term disturbances

Set On/Off heating elements to generate 3°C temperature oscillations in feed line.
Cp₂Mg concentration control in presence of disturbances

T(source) = 40°C; T(Feed line) = 50 +/-1.5°C in (a); 60 +/-1.5°C in (b)

- Feedback control results in significant reduction of composition variations in presence of disturbances
- Higher feed line temperature minimizes MO condensation
Application example: composition profiling

Use of closed loop control allows reproducible composition profiling with 1 min. response time
Conclusions

• Acoustic sensing provides very accurate measurements of metal organic concentration obtained from low VP solid source
  – Measure trace amount below 1 ppm
  – Use of resonant cavity provides good energy transfer and allows concentration measurement down to 50 Torr in sublimator
    • Interesting to obtain higher concentrations
• Use of closed loop control with acoustic sensing enables stable delivery from low vapor pressure MOCVD solid sources
  – Precursor composition control within 1% even at low precursor concentration, e.g., controlling Cp₂Mg to 1% variability at 0.01 mol % concentration in carrier gas
  – Compensate long term drifts due to source aging as well as short term drift due to source variability

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