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

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Improved precursor delivery: ESH perspectives

- Increasing variety of new precursors for advanced materials
  - Si VLSI (e.g., low and high K dielectrics), wide bandgap SC (GaN)
- Productivity and ESH metrics often affected
  - Low chemical stability, low vapor pressure liquid or solid sources, high toxicity …
- ESH benefits from improved precursor delivery:
  - Greater flexibility in chemical process design
    - Wider variety of precursors meet manufacturability constraints
  - Use of Advanced Process control
    - APC is key to higher yield and equipment effectiveness
    - Higher productivity minimizes ESH metrics such as materials utilization
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)
    - 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
Measurement of resonant frequency $F$

- 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

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

$C$: 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>
Solid source gas delivery

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

Heated lines

MFC

H₂ carrier gas

50 g. MOCVD solid source

H₂ dilution

MFC

acoustic transducer

Pressure control valve

Exhaust

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 non-linearity vs. \( 1/P \)

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

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

• **Requirements in delivery system**
  – Fixed pressure to minimize sensor drift (and potential low pressure failure)
  – Controllable precursor concentration to compensate for change in source vapor pressure (temperature or aging effects)
Effect of H$_2$ flow rates

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

• $\Sigma$ (carrier + dilution) = constant throughput
• Composition adjusted by varying H$_2$ dilution flow rate

3 E-5 mol% Standard Deviation

H$_2$ carrier flow / H$_2$ dilution flow (sccm)
P = 300 Torr
Control of Cp$_2$Mg concentration

With Cp$_2$Mg, measurement Standard Deviation = 3 E-5 mol%

- accuracy better than 1 ppm with 75 / 1 mass ratio
- can detect Cp$_2$Mg concentration change resulting from 0.1 % variation in dilution flow (under 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\(^\circ\) 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 corrected to keep composition on target
- Proportional Integral Derivative close 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
- $\Sigma (H_2 \text{ flows}) = 150$ sccm, $P = 300$ Torr
- $Cp_2Mg$ composition target = 0.01 mol% (0.3 umol/min)
Closed loop control performance

- \((C_{p_2Mg})_{\text{average}} = 0.010009 \text{ mol }\%\)
- \((C_{p_2Mg})_{\text{STD}} = 3.0 \times 10^{-5} \text{ mol }\%\)

\(C_{p_2Mg}\) 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
Cp$_2$Mg 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
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
• Use of closed loop control with acoustic sensing enables stable delivery of low vapor pressure MOCVD solid sources
  – Control of the composition within 1% even at low precursor concentration (e.g., 0.01 mol % with \( \text{Cp}_2\text{Mg} \))
  – Compensate long term drifts due to source aging as well as short term drift due to source variability
• Use of APC on reactant delivery system could significantly increase the tool productivity and reduce the precursor utilization.

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