CVD Emissions - Analysis and Treatment

Brian Goolsby
Motorola SPS
Digital DNA™ Laboratories
Acknowledgments

• Victor Vartanian – Motorola EPI
• Kim Reid – formerly of Motorola
• Joe VanGompel - BOCE
Overview

- CVD Trends Steering Characterization Needs
- Process Emissions Characterization
- Examples of CVD Processes Evaluated
- Point of Use Abatement
- Examples of CVD Emissions Abatement
- Conclusions
New Materials Everywhere!

• New materials & processes are being introduced at an unprecedented rate

• Films are thinner
• Utilization should be improved
Advanced Gate Stack

- Metal oxide gate dielectric (replaces SiO₂)
  - oxides or silicates of Ti, Ta, Sr, Zr, Hf, Al, Y, Sn, La, etc.
- Metal gate electrode (replaces doped polysilicon)
  - metals and nitrides of W, Ti, Ta, Mo, Al, Pt, etc.
- CVD process using metal-based precursors
Advanced Metallization

Copper Deposition
- Electroplating, CVD

Barrier Deposition
- PVD, CVD
- TaN, TiN, TaSiN, TiSiN, etc.
Low k Dielectrics

- Carbon-doped, porous organosilicates, porous polymers
- Spin-on
- CVD
  - organosilanes, siloxanes, halosiloxanes, silicones, etc.

\[ RC = \frac{\rho \varepsilon l^2}{td} \]

- \( \rho \) = metal resistivity
- \( \varepsilon \) = dielectric permittivity
- \( l \) = line length
- \( t \) = dielectric thickness
- \( d \) = line thickness
The Need for Analytical Data

Synthesis of Precursor

Process Enters R&D

Process Engineer

Emissions Data

EHS

Facilities / Maintenance

Internal Uses

Regulatory Body
Process Emissions Characterization

• Mass Spectrometry
  – Chamber monitoring, by-product identification
  – Emerging methods
    • high pressure sampling
    • trapping instruments
    • activated dissociation

• FTIR
  – Species quantification, high mass precursor identification, abatement efficiency determination

• Chemical-Specific
  – Limited in scope and availability, very sensitive
Analytical Sampling Schematic
Metal-based CVD Precursors and Process By-Products Detected

• Tetranitrato titanium (TN)
  – NO, NO₂, HNO₃
• Titanium tetrachloride (TiCl₄)
  – HCl
• TDMAT
  – Dimethylamine, ammonia
• Zirconium t-butoxide
  – t-butanol, isobutylene, propylene
• Hafnium t-butoxide
  – t-butanol, isobutylene, propylene
Simultaneous Unutilized Precursor and Reaction Byproduct Monitoring for TN
Mass Spectrum of Hf-t-Butoxide Process

Hf-t-Butoxide By-Product Spectrum

Ion Intensity (Amps)

He$^+$, CH$_3^+$, N$^+$/CH$_2^+$, O$^+$, H$_2$O$^+$, N$_2^+$, NO$^+$, CO$_2^+$, Hf-t-butoxide byproducts

Mass-to-Charge
Ligand By-product Reactions

Proposed reaction for:

Hf-t-butoxide

Cleavage during deposition
(surface reaction)

-CH₃ via e- impact

Isobutylene

Propylene
FTIR Spectra from TDMAT Process

Absorbance / Wavenumber (cm⁻¹)

File # 1 = TDMT0037
5/3/01  9:26 PM  Res= .5
Thu May 03 16:26:15 2001

NH₃
dimethylamine

NH₃

Y-Zoom CURSOR
5/3/01  9:26 PM  Res= .5
TDEAH

• Tetrakis diethylamino Hafnium
• Highly flammable, toxic, corrosive
• Reacts violently with water
  – forms diethylamine (toxic, extremely flammable)
• Require amine sensor (TGM) in ampoule cabinet, tool, area
Mass Spectrum During TDEAH Deposition

Shows diethyleamine by-product

Mass Spectrum from TDEAH
Handling Process Emissions

• Point of Use Abatement Devices
  – Minimize overall EHS impacts of precursors and by-products
  – Minimize personnel exposure during maintenance
  – Remove acid gases
  – Remove unreacted precursor to prevent deposition in exhaust ducts or release to environment

<table>
<thead>
<tr>
<th>DESTRUCTION OR CONVERSION</th>
<th>ENTRAINMENT</th>
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</thead>
<tbody>
<tr>
<td>-Resistive heating</td>
<td>-Chemical canister</td>
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<tr>
<td>-Flame</td>
<td>-Water scrubbing</td>
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<tr>
<td>-Catalytic</td>
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Edwards GRC

Stage 1 (S-1)
- BASE OXIDES (lime) (550 °C)
- MIXTURE OF METALS 550 °
- VAPORS

Stage 2 (S-2)
- S-1 Transfer heat into gas to reach reaction temperature
- S-1 Reacts with strong oxidizing agents (Cl₂, ClF₃) to form volatile metal halide species.
- S-1 Thermally decomposes Hydrides (SiH₄)
- S-2 Acid gases and volatile metal halides react to form harmless inorganic salts
- EX: Non-hazardous (N₂, Ar, inert gases) to duct. No acid gases.

Gas Flow
Exhaust (EX:)

TMS Heat Trace

Courtesy BOC Edwards, Joe Van Gompel
D150 GRC
Dual system
GRC Performance for TN

![GRC Performance Graph](image)

- **Intensity (Arb. Units)**
- **Time (sec)**

Graph showing the GRC Performance for TN with intensity measured in arbitrary units and time in seconds.
TiCl$_4$

- Material itself is corrosive, poisonous
- HCl is hazardous decomposition product (upon exposure to air/water)
  - monitor for HCl as TGM
- In closed CVD system, TiCl$_4$ and reaction by-products contained
  - HCl formed from unreacted TiCl$_4$ in exhaust
  - chamber maintenance becomes an issue
GRC Performance for TiCl$_4$
GRC Performance with Zr t-butoxide

- GRC in
- GRC out
- Unreacted Zr-t-butoxide
- C-H stretch
- CO₂
- H₂O
- Residual Zr-t-butoxide species
GRC Performance for Hf t-butoxide

Unreacted Hf-t-butoxide

C-H stretch

Elimination of Hf-t-butoxide species

Wavenumber (cm⁻¹)
Effect of GRC on Hf-t-Butoxide

GRC oxidizes NO to NO₂
HFTB oxidized in reactive bed

Post-GRC
Pre-GRC

CO₂
HFTB
ISOB
NO₂
NO
CDO

Heated flow tube

Sampling point - to FTIR

Water scrubber
Nitride Deposition - CDO Performance

DCS Lean process with CDO unheated

Disconnected FTIR during CDO heat-up to 640 C

Purge increases approx. 2X when CDO temp. is 650 C

DCS Lean process with CDO at 850 C
Summary

• CVD emissions typically consist of unreacted precursor and ligand materials
  – determine process efficiency
  – evaluate abatement
• Collect predictive data during R&D phase
• Work with suppliers and engineers to aid design of appropriate molecules
• Abatement solution needs to fit job
• Abatement devices can be tweaked