Addressing the EHS Issues with Advanced Gate Stack Processes

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Overview

• R&D Areas of Focus
• EHS Strategy for R&D Processes
• Process Emissions Characterization
• Examples of CVD Processes Evaluated
• Point of Use Abatement
• Summary
New Materials Everywhere!

New materials & processes are being introduced at an unprecedented rate
Advanced Gate Stack

- Metal oxide gate dielectric (replaces SiO$_2$)
  - 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
EHS Concerns

• Employee exposure
  – chemical handling
  – accidental release/leak
  – chamber/exhaust maintenance

• Impacts to infrastructure
  – drain lines, exhaust lines

• Material compatibility
  – potential reaction with other components
  – materials of construction

• Environmental impact
EHS Strategy

- EHS review required for ALL new materials
- Specific tool, process, tool location, storage location, usage rate
- Specific point of contact
- Ensure compatibility with tool exhaust/drain and sufficient TGM
- EHS considers potential for exposure and associated hazards
- EHS can require tool/procedure modifications if necessary
EHS Strategy (cont)

• Thorough review of MSDS
  – chemical components - adducts, solvents, etc.
  – toxicity, flammability, reactivity (if known)
  – material incompatibilities
    • tool components, co-flow materials, etc.
  – predicted reaction products
  – special handling procedures
  – recommended PPE
  – component for TGM

• Available supplier data, other data sources
  – TOMES, “like” materials or chemical families, web surfing, etc.
EHS Strategy (cont.)

• Process hazard analysis
  – how material will be used, potential for exposure, etc.
• TGM based on breakdown product(s)
  – often no specific sensor for precursor itself
• Handle with conservative PPE strategy
• Operate under engineering control only
• Monitor process emissions - QMS, FTIR, RGA, other
  – reaction by-products & unreacted precursor
  – residual precursor/by-product in chamber
• POU abatement for process emissions where needed
  – highly toxic/flammable material, by-product, or co-flow material (e.g., silane)
• Special chamber maintenance strategy
Monitoring Strategy

• Detect release/leak of hazardous gas/vapors before concentration reaches dangerous level
• For toxic gases, warn at 1/2 TLV (or less), alarm (with automatic source shut down) at TLV
• For flammable gases, warn at 10% of LEL and alarm at 20% LEL
• Can monitor in gas cabinet, valve box, tool (inside enclosure) and area (work, utility, subfab)
• Various types of monitors
  – specific compound
  – general class (flammable, mineral acid, hydride, etc.)
• May monitor breakdown product
Chamber Maintenance Strategy

- Conservative “worst case” procedure for first chamber opening after process has been run
- Clear area around chamber and sub-fab
- Response team on stand by
- Supplemental exhaust (elephant trunk) if available
- Maintenance personnel in full PPE, SCBA
- TGM sensor point in chamber/area if available
- IH personnel and area monitoring
- Monitor emissions during purge
  - ensure no signal for residual precursor, by-product
- Special wipes & spent wipe container if necessary
  - wipes may be analyzed
Regulatory Issues

- TSCA inventory status
  - must be listed or have low volume exemption to be used in manufacturing
  - low volume exemption = only 10,000 kg/yr can be manufactured by all suppliers collectively
  - Listing process is data intensive, lengthy and expensive
  - Promising materials can transfer to manufacturing quickly
EHS Data Collection

• Evaluation CVD precursor candidates:
  – TN [Ti (NO$_3$)$_4$]
  – TiCl$_4$
  – TDMAT
  – Zr t-butoxide and Hf t-butoxide
  – TDEAH
• TiCl$_4$, TDMAT somewhat characterized, TSCA listed
• Zr t-butoxide and Hf t-butoxide, TDEAH not TSCA listed
• TN newly synthesized, not TSCA listed
  – worked with supplier to determine properties and potential hazards (e.g., upon exposure to air or water, solvents, thermal decomposition)
Process Emissions Characterization

- **QMS**
  - foreline monitoring, by-product identification

- **ITMS**
  - post pump, species identification & reaction pathway determination

- **FTIR**
  - species quantification, high mass precursor identification, abatement efficiency determination
Analytical Sampling Schematic

- Process Chamber
- Precursor out
- He carrier
- Foreline
- RGA Port
- N₂ purge in
- Blower
- Dry Pump
- QMS
- FTIR 2 (15 m)
- ITMS
- GRC Dual Gas Reactor Column
- Scrubbed Exhaust
- Heated extraction lines
- FTIR 1 (6 m)
Metal-based CVD Precursors and Process By-Products Detected

- Tetranitro titanium (TN)
  - NO, NO\textsubscript{2}, HNO\textsubscript{3}
- Titanium tetrachloride (TiCl\textsubscript{4})
  - HCl
- TDMAT
  - Dimethylamine, ammonia
- Zirconium t-butoxide
  - t-butanol, isobutylene
- Hafnium t-butoxide
  - t-butanol, isobutylene
Mass Spectrum of Hf-t-Butoxide Process
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
TiCl$_4$ Chamber Maintenance

- Purged system prior to opening
  - no HCl or TiCl$_4$ signal detected
- HCl detected in “elephant trunk” when chamber first opened
  - indicates residual HCl or TiCl$_4$ in chamber or lines that reacted upon exposure to air
  - further studies to determine adequate purging
TN \([\text{Ti(NO}_3\text{)}_2]\)

- TN (solid) is corrosive, strong oxidizer, reacts with moisture to form \(\text{HNO}_3\) (exothermic)
- \(\text{NO}_x\) is CVD reaction by-product
- Reacts with IPA to form \(\text{NO}_x\)
  - Standard chamber wipe down solution of 10% IPA in water NOT recommended -- water only
- No degradation with standard o-ring materials
Simultaneous Unutilized Precursor and Reaction Byproduct Monitoring for TN
TN Chamber Maintenance

- Purged thoroughly
  - no NO\textsubscript{x} or TN signal noted
- No issues with chamber opening (no detections)
- No issue with water wipe down (minimal temperature rise)
TDMAT

- Tetrakis (dimethylamino) titanium
- Highly flammable, corrosive, odorous liquid
- Reacts violently with water
  - forms dimethylamine (toxic, extremely flammable) and NH$_3$ by-product
- Require amine sensor (TGM) in ampoule cabinet, tool, area
- Require point of use abatement for process emissions
FTIR Spectra from TDMAT Process

Absorbance / Wavenumber (cm⁻¹)
File #1 = TDMAT0037

Thu May 03 16:26:15 2001

Absorbance / Wavenumber (cm⁻¹)
File #1 = TDMAT0037

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Thu May 03 16:26:15 2001
TDMAT Chamber Maintenance

- TGM sensor point in chamber detected dimethylamine at 7.5 ppm or greater
  - > than TLV (5 ppm), possibly greater than PEL (10 ppm)
- Special wipes for chamber wet clean
  - cleanroom polypropylene
  - use 100% IPA - NO WATER
- Supplemental exhaust to be installed
TDEAH

• Tetrakis dimethylamido 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 from TDEAH

Mass Spectrum During TDEAH Deposition

Shows diethylamine by-product
Handling Process Emissions

• Point of Use Abatement Device
  – Minimize overall EHS impacts of precursors and by-products
  – Minimize personnel exposure during maintenance
  – Remove unreacted precursor to prevent deposition in exhaust ducts or release to environment
  – Remove/destroy hazardous by-products or co-flow materials
Hot Bed Dry Scrubber

- **Stage 1 (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: Nonhazardous (N₂, Ar, inert gases) to duct. No acid gases.

- **Stage 2 (S-2)**: Mixtures of metals (550 °C) result in vapors. Base oxides (lime) (550 °C) transfer heat into gas to reach reaction temperature.
Thermal Destruction Unit

Exhaust Gases

N₂
CDA

Heater Element

850 C

Treated Exhaust

water spray nozzle

Cooling / Scrubbing

water spray nozzle

water spray nozzle
Hot Bed Dry Scrubber Performance for TN

Unit Performance

Intensity (Arb. Units)

Time (sec)

TN In

TN out
Hot Bed Dry Scrubber Performance for TiCl₄

Absorbance / Wavenumber (cm⁻¹)

HCl

Unit in

Residual H₂O

CO₂

Unit out

File # 2 = TICL0056

1/29/01  10:59 PM  Res= .5
Hot Bed Dry Scrubber
Performance with Zr t-butoxide

Unit in
Unreacted
Zr-t-butoxide

C-H stretch

Unit out
Residual Zr-t-butoxide species

Absorbance

C-H bend

Wavenumber (cm⁻¹)

File # 1 = Z:\TOOLST~1\UDCL03\ZRTB0227.SPC 17009 Rows

C-H stretch

H₂O

CO₂

H₂O

CO₂
Hot Bed Dry Scrubber
Performance for Hf t-butoxide

Absorbance / Wavenumber (cm⁻¹)

Unreacted Hf-t-butoxide

Unit in

C-H stretch

Unit out

Elimination of Hf-t-butoxide species

H₂O
Thermal Destruction Unit Performance for TDMAT

FTIR spectra of TDMATTiN Deposition Process

Absorbance / Wavenumber (cm⁻¹)

File # 2 = C0089
12/21/01 5:55 PM Res=None

121C 600T 10m cdo
Summary

• EHS Strategy must focus on entire process, not just the new material itself
• Must employ very conservative procedures until process is thoroughly characterized
• Collect as much data as possible in R&D phase
• Work with suppliers to collect additional data as needed to transfer to manufacturing