PFC Emissions Monitoring by FT-IR in LCD Manufacturing Processes

MIDAC Corporation
Overview

- FT-IR monitoring to reduce PFC emissions in Semiconductor Facilities
- Applying FT-IR Monitoring to LCD manufacturing process
- Efforts for reducing PFC emissions in Asian Countries
FT-IR monitoring to reduce PFC emissions in Semiconductor Facilities

Every semiconductor manufacture in the world is making efforts to monitor and reduce PFC emissions from their facilities based on an agreement of the World Semiconductor Council.

The agreement aims at over-10% reduction of the amount of total PFC emission compare to that of 1995 by 2010.

For PFC emissions monitoring, they already have the established testing methodologies such as “Guidelines for Environmental Characterization for Semiconductor Equipment” presented by International SEMATECH.
PFC Emission Calculation based on IPCC’s Formula (1)

\[
[Emission\ of\ FC_i] = (1-h) \sum p(F_{ci,p})[(1-C_{i,p})*(1-A_{i,p} \cdot D_{i,p})*GWP_{i} + B_{i,p} \cdot (1-A_{i,p} \cdot D_{CF4,p}) \cdot GWP_{CF4}
\]

Where:
\(i\) = FC gas (NF3, CF4, etc.)
\(p\) = Process Type (Etching or CVD chamber cleaning)
\(F_{Ci,p}\) = Mass of gas I fed into process type p (kg of gas i)
\(A_{i,p}\) = Fraction of gas volume fed into processes with emission control technologies
\(C_{i,p}\) = Use rate (fraction destroyed or transformed) for each gas i and process type p
\(D_{i,p}\) = Fraction of gas i destroyed by emission control technology
\(B_{i,p}\) = Fraction of gas i transformed into CF4 for each process type
# PFC Emission Calculation based on IPCC’s Formula (2)

<table>
<thead>
<tr>
<th>Method</th>
<th>Process</th>
<th>Emission factor (Ci, Bi, di)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tier 1</td>
<td>No distinction</td>
<td>Default Value</td>
</tr>
<tr>
<td></td>
<td></td>
<td>di = 0</td>
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<tr>
<td>Tier 2a</td>
<td>Small subsets of processes or tools</td>
<td>Company-Specific or Fab –Specific</td>
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<tr>
<td></td>
<td></td>
<td>measurement data</td>
</tr>
<tr>
<td>Tier 2b</td>
<td>CVD and Etching (only process types)</td>
<td>Default Value or Company (Fab)-Specific</td>
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<td>measurement data</td>
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<tr>
<td>Tier 2c</td>
<td>No distinction</td>
<td>Default Value</td>
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</table>
Introduction of “Guidelines for Environmental Characterization for Semiconductor Equipment” (1)

This document has been designed to provide guidance to equipment and abatement suppliers on how to characterize the environmental performance of their semiconductor processes.

The characterization must include quantification of both air and water emissions.

It also describes tool types and types of emission information required for each tool type.
For Air Emissions, emissions testing methods must include a volume balance that accounts for >90% of fluorine, chlorine, and bromine.

In order to calculate mass balance of above compounds, specified emission compounds should be quantified for a particular process chemical. There is a list for Target Compounds (For details, refer to the section 2.1 of “Guidelines for Environmental Characterization for Semiconductor Equipment”)

The testing methods must follow an approved method (Fourier transform infrared [FT-IR] or quadruple mass spectroscopy [QMS])
**Epson method datasheet**

Designed to facilitate FT-IR measurement complying with “Guidelines for Environmental Characterization for Semiconductor Equipment”. It was originally created using MIDAC reference libraries, “Standards”.

<table>
<thead>
<tr>
<th>Molecular Formula</th>
<th>Target Compound</th>
<th>Measure Range</th>
<th>Libraries and Wave Number Ranges (cm⁻¹)</th>
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<tbody>
<tr>
<td>CF₄</td>
<td>Process Chemical</td>
<td>~60ppm-m</td>
<td>CF₄_2A, _1A, 2CF429, 59(1230–1305)</td>
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<tr>
<td>CHF₃</td>
<td>Target Emission</td>
<td>~60ppm-m</td>
<td>TFM_7A(1111–1215), _1A(1316–1437)</td>
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<tr>
<td>C₂F₄</td>
<td></td>
<td>~46ppm-m</td>
<td>2C₂F₄, _1A(1161–1212)</td>
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<td>C₂F₆</td>
<td>Target Emission</td>
<td>~150ppm-m</td>
<td>C₂F₆_7A(1218–1290), _1A, _2A(1082–1136)</td>
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<td>C₃F₈</td>
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<td>~525ppm-m</td>
<td>C₃F₈_31A, 19A, 11A(956–1061)</td>
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<td>C₄F₈</td>
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<td>~150ppm-m</td>
<td>2C₄F₈, _1A(920–1020)</td>
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<tr>
<td>SF₆</td>
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<td>NF₃</td>
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<td>2NF₃_31, _20(832–960)</td>
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<td>CO</td>
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<td>CO_31A(2143–2246)</td>
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<td>CO₂</td>
<td>Target Emission</td>
<td>~66ppm-m</td>
<td>CO₂_51A, _1A, _2A(2280–2390)</td>
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<td>COF₂</td>
<td>Target Emission</td>
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<td>COF₂_55A, _41A(1790–2015)</td>
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<td>Target Emission</td>
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<td>OF₂_17S(755–1012)</td>
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<td>SiF₄</td>
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<td>SiF₄_38A(1000–1058)</td>
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<td>SOF₂</td>
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<td>~90ppm-m</td>
<td>SOF₂_17S(712–860)</td>
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<td>~130ppm-m</td>
<td>2SO₂F₂(1445–1545)</td>
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<td>~50–500ppm-m</td>
<td>NO_2B(1757–1990)</td>
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<td>~140ppm-m</td>
<td>NO₂_19A(1525–1791)</td>
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<td>N₂O</td>
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<td>~150ppm-m</td>
<td>2N₂O_10, _8(1216–1338)</td>
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Configuration for Monitoring CVDs

- Sample extracted from a CVD exhaust line
- MFC
- Sample going back to abatement
- Purge N2
- Pressure transducer for a gas cell
- FT-IR Main Body
- Purge Nitrogen Outlet
- Short path Cell
- Purge Nitrogen Inlet

CVD Chamber

Scrubber

Pump

Inlet

Purge Nitrogen

Outlet
Configuration for Monitoring Scrubbers

- Sample going back to abatement
- FT-IR Main Body
- CVD Chamber
- Scrubber
- Scrubber
- MFC
- Pump
- Pressure transducer for a gas cell
- Purge Nitrogen Outlet
- Purge Nitrogen Inlet
- Short path Cell
- Post scrubber Sample
- Sample extracted from before a Scrubber
- Purge N2
Measurable concentration ranges of major PFC compounds for each cell path length

<table>
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<tr>
<th></th>
<th>1cm Cell</th>
<th></th>
<th>10cm Cell</th>
<th></th>
<th>3m Cell</th>
<th></th>
<th>20m Cell</th>
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<td></td>
<td>MDL PPM</td>
<td>UDL PPM</td>
<td>MDL PPM</td>
<td>UDL PPM</td>
<td>MDL PPM</td>
<td>UDL PPM</td>
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<td>CF4</td>
<td>3</td>
<td>40000</td>
<td>0.3</td>
<td>4000</td>
<td>0.010</td>
<td>133</td>
<td>0.002</td>
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<tr>
<td>CHF3</td>
<td>14</td>
<td>40000</td>
<td>1.4</td>
<td>4000</td>
<td>0.047</td>
<td>133</td>
<td>0.007</td>
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<td>C2F6</td>
<td>10</td>
<td>40000</td>
<td>1</td>
<td>4000</td>
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<td>133</td>
<td>0.005</td>
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<td>C3F8</td>
<td>5</td>
<td>50000</td>
<td>0.5</td>
<td>5000</td>
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<td>60</td>
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<td>0.014</td>
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<td>30000</td>
<td>50</td>
<td>3000</td>
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<td>10</td>
<td>13500</td>
<td>1</td>
<td>1350</td>
<td>0.033</td>
<td>45</td>
<td>0.005</td>
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<td>COF2</td>
<td>100</td>
<td>10000</td>
<td>10</td>
<td>1000</td>
<td>0.333</td>
<td>33</td>
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<td>HF</td>
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<td>72000</td>
<td>12.5</td>
<td>7200</td>
<td>0.417</td>
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<td>SiF4</td>
<td>45</td>
<td>5700</td>
<td>4.5</td>
<td>570</td>
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<td>SO2</td>
<td>15</td>
<td>12600</td>
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<td>110</td>
<td>5000</td>
<td>3.667</td>
<td>167</td>
<td>0.550</td>
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<td>NO2</td>
<td>140</td>
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<td>14</td>
<td>1400</td>
<td>0.467</td>
<td>47</td>
<td>0.070</td>
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<td>N2O</td>
<td>360</td>
<td>15000</td>
<td>36</td>
<td>1500</td>
<td>1.200</td>
<td>50</td>
<td>0.180</td>
</tr>
</tbody>
</table>

Since above values are theoretically calculated based on Minimum and Upper Detection Limits of 1m Cell, Limits can change depending on measurement environments or if gasses are mixed.
MIDAC I4000 Series

FT-IR Main Body

Pressure Transducer

3m Cell

PC

Pressure and Temperature Controller
MIDAC I4000 Series Dual Cell Model

FT-IR Main Body

10cm Cell

3m Cell
QMS & FTIR Setup for Exhaust Monitoring

A : Main Vacuum Pump
B : Sample Pump
\# : Shut-off valve
C : Calibration Gases
D : SF6 gas standard
E : Mass Flow Controller
F : Exhaust line

CVD

QMS

B

N₂

C / D

FTIR

E

F
QMS and FTIR as Complementary Tools

FT-IR

- Advantages:
  - On Site Quantitative Analysis of all PFCs and most of the HAPs
  - Non-destructive and Real-Time Analysis
  - Relatively low cost
  - Off-site calibration and periodic on-site response checks
- QA(Quality Assurance)/QC(Quality Control) Check:
  - Cell path length
  - Linearity check
- Disadvantages:
  - Cannot detect homonuclear diatomic species (Ex: F$_2$, Cl$_2$ etc.)
QMS and FTIR as Complementary Tools

QMS

❖ Advantages:
  ■ On-Site Quantitative Analysis of all PFCs and HAPs
  ■ Non-destructive and Real-Time Analysis
  ■ Wide Dynamic Range

❖ QA (Quality Assurance)/QC (Quality Control) Check:
  ■ Calibration drift (depends on nature of exhaust stream)
  ■ Periodic on-site calibration checks

❖ Disadvantages:
  ■ Can monitor only pre-selected target species
  ■ Needs to be calibrated on-site for all target gases
  ■ Any silicon based sources should be avoided to transport exhaust gases into QMS
Linearity Check for QMS & FTIR

QMS Linearity check
\[ y = 16.675x \]
\[ R^2 = 0.9999 \]

FTIR Linearity Check
\[ y = 16.227x \]
\[ R^2 = 0.9988 \]

Note: ppmv means ppm by volume
QMS and FTIR Emission Analysis for $C_3F_8$ Chamber Clean Recipe

**QMS-Data**

- Concentration (PPM)
- Time (hr:min)

**FTIR-Data**

- Concentration (PPM)
- Time (hr:min)
QMS analysis of $F_2$ from $C_2F_6$ and $C_3F_8$ chamber cleans

Note: a.u. means arbitrary unit
Applying FT-IR Monitoring to LCD manufacturing process
Position Paper Regarding PFC Emission Reduction Goal

Emission reduction for PFCs proposed by the World LCD Industry Cooperation Committee (WLICC) Working Group 1 (WG1) has been approved by members of the WLICC (the LCD Industries Research Committee in Japan, or LIREC/JEITA, the Environment Association of LCD in Korea, or EALCD/EDIRAK, and the Taiwan TFT-LCD Association, or TTLA) at the second WLICC main committee meeting held in Taiwan on January 20th, 2002.
Consensus on the PFC emission reduction goal

LIREC, EALCD and TTLA have reached a consensus to reduce the aggregate absolute emissions of PFCs from the TFT-LCD fabrication facilities to less than 0.82 MMTCE (million metric tons of carbon equivalent) by the year of 2010.
Challenge against PFC Emission Reduction Activities in LCD Industry

- The target emissions correspond to approximately 0.013% of global climate change gas emissions of the world for 1998. Unless countermeasures are taken, the aggregate emissions in 2010 might reach more than ten times of the target emissions and exceed the target emissions of the LCD industry.

- LCD companies are now using Tier2C (Default Value) of IPCC calculation formula, resulting in wide gap between our estimate and actual data.

(Big Challenge!) Considering above situations, shift from Tier 2C to Tier 2A or Tier 2B is expected, which means increase of actual measurement in each company or fab.
Problems in applying PFC Emissions Monitoring by FT-IR to LCD Industry

- Lower FT-IR placement in LCD companies than Semiconductor
- Inexperienced FT-IR operators, or even worse, lack of operators.
Where should we monitor by FT-IR in a fab?

- Gasses
- Equipment
- Abatement Equipment
- POU Scrubber
- Exhaust

FT-IRs are not required if recipes are given from suppliers
How many units FT-IR are required for a single fab?

[Example]

For an intermediate level FT-IR operator, a single point measurement will take two hours with single (roaming) FT-IR spectrometer …

Of course, he can not fully engage himself for monitoring, so maybe 2 or 4 hours a day.(1 points or 2 points per day)

Assuming that the fab has 300 monitoring points and he should monitor turn by turn, it will take 300 or 150 days to complete monitoring one cycle of total 300 points…

What if your fab had more monitoring points, or new regulation requires you to monitor your points more frequently?
Proposal for usage of sampling manifold FT-IR

1 CVD line takes 10 minutes * 12 = 120 minutes for monitoring a dozen CVDs with just two FT-IR with one person! Combination of these sets enables to finish monitoring over 300 points in a fab for a month or even a week!
Cost for purchasing FT-IR and piping

Cost for 12 points...

1. One FT-IR (For higher or lower concentration) $100,000～$120,000
2. One twelve line manifold $5000
3. One Quad Head Pump (to draw sample to FT-IR) $3000
4. Cost for piping 12 lines depends on fab
5. Flexibly using roaming dual cell FT-IR! $160,000
   (Use where pipe length are too long)

Ex. Measure 96 points (Long, Short each 48 points) with manifolds and other 24 points with dual cell

Cost = 8*[(1)+(2)+(3)+(4)] + (5) = $1,104,000 + Piping costs
↑ Explosion Proof Enclosure

↓ Example of manifold usage for monitoring low level concentration gasses
Easy software for entry operator

User Friendly

MIDAC experts will give you powerful support.

Reliable Results

AutoQuant Pro™
SOFTWARE FOR GAS PHASE INFRARED SPECTRAL ANALYSIS
1) QMS & FTIR for On-line Semiconductor Exhaust Characterization
   by M. Kataoka*, S. Kesari***Sumitomo-3M, **3M Company

2) Position Paper Regarding PFC Emission Reduction Goal
   by World LCD Industry Cooperation Committee

3) Guidelines for Environmental Characterization
   for Semiconductor Equipment
   by International SEMATECH