Diagnostics and modelling of atmospheric pressure chemical vapour deposition reactors

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# Contents

## List of Figures
- 7

## List of Tables
- 14

## Acronyms and Symbols
- 15

## Abstract
- 18

## Declaration
- 19

## Copyright Statement
- 20

## Acknowledgements
- 21

## The author
- 22

## 1 Introduction

1.1 Thin solid films ........................................... 23
1.2 Tin oxide thin films ......................................... 26
1.3 Coating of large area substrates .............................. 28
1.4 APCVD manufacturing of tin oxide ........................... 29
1.5 Challenges in APCVD processes ............................... 29
1.6 APCVD process monitoring and control ....................... 30
   1.6.1 Challenges in APCVD process monitoring .......... 30
   1.6.2 Proposed methodology for APCVD process monitoring ... 33
1.7 Modelling of APCVD processes ................................ 35
1.8 The thin film coating techniques and market .................. 36
   1.8.1 CVD in comparison to other thin film technologies .... 36
   1.8.2 Thin film market ...................................... 37
1.9 Summary .................................................... 41
1.10 Aims of this thesis .......................................... 43

## 2 Literature review

2.1 Introduction .................................................. 44
2.2 Chemical vapour deposition ................................... 45
   2.2.1 Principles of chemical vapour deposition ............ 45
2.2.2 Chemical vapour deposition reactors ........................................ 47
2.3 Transparent conductive oxides ................................................. 49
2.4 Chemical vapour deposition of tin oxide ..................................... 51
  2.4.1 Deposition temperature .................................................. 54
2.5 Optical monitoring on chemical vapour deposition processes ............ 55
2.6 The application of computational fluid dynamics for chemical vapour
deposition .............................................................................. 58

3 Methodology .................................................................................. 62
  3.1 Introduction ............................................................................. 62
  3.2 Fundamentals of spectroscopy ..................................................... 63
    3.2.1 The electromagnetic spectrum ............................................ 63
    3.2.2 Vibrational-rotational spectroscopy .................................... 65
    3.2.3 Beer-Lambert law ............................................................ 68
    3.2.4 Broadening of spectral lines and lineshape functions .............. 71
    3.2.5 Semiconductor detectors .................................................. 74
    3.2.6 Optical fibres .................................................................... 75
  3.3 Fundamentals of diode laser absorption spectroscopy at atmospheric
  pressure ...................................................................................... 76
  3.4 Fundamentals of FTIR spectroscopy ............................................. 79
    3.4.1 Michelson interferometer ................................................... 79
    3.4.2 Apodization ....................................................................... 82
    3.4.3 Phase correction ............................................................... 84
  3.5 Infrared diffraction grating spectrometry ....................................... 85
  3.6 Computational Fluid Dynamic simulations ..................................... 87
    3.6.1 The Fluent CFD code ........................................................ 88
    3.6.2 Ideal gas diffusion ............................................................. 89
    3.6.3 Viscosity .......................................................................... 93
    3.6.4 Thermal conductivity ......................................................... 93
    3.6.5 Thermal diffusion ............................................................. 95
    3.6.6 Density ............................................................................ 95
    3.6.7 Chemical reactions ........................................................... 96
  3.7 Summary .................................................................................... 97

4 Experimental equipment .................................................................... 98
  4.1 Introduction ............................................................................. 98
5 Monitoring of APCVD process stability through \textit{in-situ} and \textit{in-line} spectroscopy \hfill 116
5.1 Introduction \hfill 116
5.2 Potential material savings through \textit{in-line} and \textit{in-situ} process monitoring \hfill 117
5.3 Monitoring of process stability through \textit{in-situ} near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase \hfill 117
5.3.1 \textit{In-situ} laser absorption monitoring measuring arrangement \hfill 119
5.3.2 Measurement procedures and results \hfill 121
5.3.3 \textit{In-situ} measurements with moving substrate \hfill 122
5.3.3.1 Monitoring results \hfill 122
5.3.3.2 Correlation of film thickness to HCl gas phase concentration \hfill 128
5.3.4 \textit{In-situ} measurements with stationary substrate \hfill 130
5.3.4.1 Variation of the bubbler flow rate \hfill 131
5.3.4.2 Variation of the oxygen flow rate \hfill 134
5.3.4.3 HCl concentration during stepwise reactor start-up \hfill 134
5.4 Combination of infrared grating absorption and near infrared laser absorption spectroscopy for \textit{in-line} and \textit{in-situ} process monitoring and control \hfill 135
5.4.1 Simulation of blockages through by-passing of the bubbler \hfill 137
5.4.2 Simulation of blockages by stopping the bubbler feed \hfill 138
5.4.3 Concentration variation through temperature variations in the bubbler \hfill 139
5.5 Summary \hfill 140
6 Thermal decomposition pathway of the Monobutyl tin tri-chloride precursor

6.1 Introduction ................................. 142
6.2 Comparison of novel mid-infrared fibre optic cable and conventional mirror arrangements for in-situ FTIR monitoring in APCVD reactors 142
6.3 Monitoring the decomposition of MBTC *in-situ* ......................... 145
  6.3.1 Experimental procedure .................................. 147
  6.3.2 Results .............................................. 148
6.4 Decomposition species of MBTC .................................. 149
  6.4.1 Experimental procedure .................................. 149
  6.4.2 Results .............................................. 151
  6.4.2.1 Thermal decomposition of MBTC ...................... 151
  6.4.2.2 Thermal decomposition of MBTC and oxygen .......... 157
  6.4.2.3 Thermal decomposition of MBTC, oxygen and water 162
6.5 Possible reaction pathway of tin oxide deposition from MBTC, oxygen and water .............................................. 162
6.6 Summary ............................................ 163

7 Computational Fluid Dynamics modelling of an APCVD thin film deposition reactor

7.1 Introduction ...................................... 165
7.2 Model geometry and meshing .................................. 167
  7.2.1 Model geometry ..................................... 167
  7.2.2 Meshing ............................................. 170
  7.2.2.1 Meshing fundamentals ............................. 170
  7.2.2.2 Meshing of the APCVD reactor model .............. 170
7.3 Reactor chemistry ..................................... 172
7.4 Computation ........................................ 174
7.5 Simulation results ..................................... 176
7.6 Comparison to experimental data ................................ 183
7.7 Summary ............................................ 186

8 Discussion, further work and conclusions

8.1 Discussion ....................................... 188
  8.1.1 Monitoring of APCVD process stability through *in-line* and *in-situ* spectroscopy .......................... 188
Contents

8.1.2 Calculation of material savings through optical monitoring . . 189
8.1.3 Thermal decomposition studies of the MBTC precursor . . . . 190
8.1.4 Computational fluid dynamics modelling of an APCVD thin
film deposition reactor . . . . . . . . . . . . . . . . . . . . . . 191
8.2 Further work . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 192
8.3 Conclusions . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 193

Bibliography 195

A Publications (in preparation) 209
Further publications in preparation . . . . . . . . . . . . . . . . . . . . . 213

B FTIR spectra 214

C Programming codes 221
C.1 R-code for NIR-LAS post-processing . . . . . . . . . . . . . . . . . . . 221
C.2 R-code for FTIR post-processing . . . . . . . . . . . . . . . . . . . . 227

Total word count: 37799
List of Figures

1.1 Basic steps of a CVD process for thin film deposition from two precursors \[24\]
1.2 Schematic of the growth regime depending on temperature and pressure \[26\]
1.3 Principle structure of an amorphous silicon solar cell. The rough surface morphology of the tin oxide layers causes the incident light to be trapped in the solar cell \[27\]
1.4 Cross sections of two common types of on-line APCVD coating systems \[28\]
1.5 Schematic of tin oxide deposition on a float glass line with comparison of a standard control feedback loop and a potential optical monitoring supported feedback loop with faster control response \[32\]
1.6 European Union photovoltaic capacity market development \[39\]
1.7 Development of solar cell efficiencies 1976 – 2014. Figure from NREL (National renewable energy laboratory, U.S. Department of Energy) \[40\]
2.1 Growth rate (logarithmic) as a function of the growth temperature \[47\]
2.2 Two common CVD reactor types for vacuum coatings. The horizontal tube reactor can be operated at atmospheric pressure as well \[48\]
2.3 High throughput APCVD coater with moving substrate \[49\]
2.4 Comparison between DMTC and MBTC APCVD film growth rates. Refer to the references for process conditions \[53\]
2.5 Temperature dependency of the growth rate for varied water content. MBTC concentration 1 mol%, oxygen to nitrogen ration: 0.2 \[55\]
2.6 Setup to measure in-situ film thickness and gas phase composition \[57\]
2.7 Concentration of HCl monitored at two points on an roll-to-roll AP-CVD process with laser absorption spectroscopy \[58\]
2.8 Comparison of experimental data to the original model mechanism and the surface reaction rate adjusted mechanism \[61\]
3.1 The electromagnetic spectrum \[64\]
3.2 Vibrational modes of CO\(_2\) and HCl \[65\]
3.3 Excitation from the vibrational rotational ground state \(\psi = 0\) to the first excitation state of the HCl molecule \(\psi = 1\) with rotational states \(j\) \[67\]
3.4 Spectrum of hydrogen chloride in the mid-infrared region (simulated by spectralcalc) \[68\]
3.5 FTIR spectrum of MBTC and Butane \[68\]
List of Figures

3.6 Photon energy transfer and principle of the Beer-Lambert law . . . . 69
3.7 Energy transition, line shape with kernel, wings and full width at half
maximum . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 72
3.8 Comparison of the Gaussian and Lorentzian lineshape function with
identical FWHM (indicated by arrows) . . . . . . . . . . . . . . . . . 73
3.9 Detectivity over wavelength of popular infrared detectors . . . . . . 75
3.10 Schematic of an optical fibre . . . . . . . . . . . . . . . . . . . . . . 76
3.11 Basic structure of a Vertical Cavity Surface Emitting Laser diode and
detailed view of the energy band structure in the active region . . . . . 78
3.12 Schematic of a Michelson interferometer . . . . . . . . . . . . . . . . 80
3.13 Fourier transform of a single infinite cosine function (a) results into a
single frequency (b) . . . . . . . . . . . . . . . . . . . . . . . . . . . 81
3.14 Truncation of the continuous wave function through the sinc function
and the resulting Fourier transform with the broadened peak and
superimposed sine-wave components . . . . . . . . . . . . . . . . . . . 83
3.15 Comparison of the Norton-Beer apodization function to the sinc function 83
3.16 Littrow monochromator with spherical mirror and array detector element 86
3.17 Schematic plot of the Lennard-Jones potential energy $\phi(r)$. $\sigma$ is the
characteristic length and $\epsilon$ the minimum energy parameter. $r$ is a
radius of molecular length. . . . . . . . . . . . . . . . . . . . . . . . . 92

4.1 Schematic setup of the coating systems. Feed section consists of
bubbler with MBTC on hotplate, nitrogen as carrier gas, oxygen and
water as reactants. Water is injected by a syringe pump. Coating head
has a laminarizer, an inlet slot and extraction ducts. The substrate
sits on a translating heated susceptor block. Pipes past the flow meters
are tape-heated to 130°C . . . . . . . . . . . . . . . . . . . . . . . . . . . 100
4.2 Bottom and side view of the APCVD reactor head with expected gas
flow patterns . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 101
4.3 Translational movement of the susceptor for one pass of the substrate
under the coating head. Speed can be adjusted and is commonly set
to 3mm/sec . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 101
4.4 Simulated transmittance spectrum of the first overtone of hydrogen
chloride (1.7µm) in the near-infrared . . . . . . . . . . . . . . . . . . . . 102
List of Figures

4.5 Setup of the laser monitoring system. Laser is controlled by a data acquisition board connected to a control PC. Laser launch and detector have full five axes adjustability. Rotation around x-, y- and z-axis and translation in z- and y-direction ........................................ 103
4.6 Signal recorded by the photo detector ........................................ 104
4.7 Signal generated by the etalon over scan points and wavenumber and highlighted positive peak positions ........................................ 105
4.8 Raw scan signal \( I \) with fitted third order polynomial background \( I_0 \) . 107
4.9 Extracted absorption peak of HCl and fit of a Lorentzian function . 107
4.10 Screenshot of the R-code processing recorded HCl spectra within the R-studio programming environment ........................................ 108
4.11 Comparison of 13.5\% beam diameters recorded with a Thorlabs BP109-IR2 in increasing distance from the lens ................................. 109
4.12 Schematic of the experimental setup for the measurement of MBTC decomposition products. Red dashed line indicates the infrared beam path from the FTRI instrument, through the optical cell to the MCT detector .......................................................... 110
4.13 Setup and schematic of the infrared grating spectrometer .............. 113
4.14 Infrared transmission spectrum of MBTC (FTIR, 1 cm\(^{-1}\) resolution). Marked peak (red) was selected for monitoring with the grating spectrometer ................................................................. 114
4.15 Grating spectrometer calibration data ........................................ 115

5.1 Cross section of the lab scale reactor with arrows illustrating the reactive gas mixture, the assumed air flow pattern and beam positions119
5.2 In-situ laser monitoring arrangement ........................................ 121
5.3 Typical monitoring result obtained from six substrate passes. A single pass is highlighted (red). A 10 point moving average smoothing was applied. ................................................................. 123
5.4 HCl concentration profile during steps of the process .................... 124
5.5 Absorption of HCl, measured on 11 positions in the CVD reactor during six substrate passes (Set 1) ........................................ 126
5.6 Absorption of HCl, measured on 11 positions in the CVD reactor during six substrate passes (Set 2) ........................................ 127
5.7 Variation of SnO\(_2\) film thickness for identical flow rates of two experimental sets ................................................................. 128
List of Figures

5.8 Mean integrated absorbance of HCl at various locations in the APCVD reactor ........................................... 129
5.9 Film thickness over integrated absorbance ................................................................. 130
5.10 Film thickness over integrated absorbance. Linear fitting function for prediction of film thickness derived from selected monitoring points .............................. 130
5.11 Monitoring of HCl at position 9 during variation of the bubbler nitrogen flow rate .............................................. 131
5.12 Monitoring of HCl at position 5 during variation of the bubbler nitrogen flow rate .............................................. 132
5.13 Monitoring of HCl at position 3 during variation of the bubbler nitrogen flow rate .............................................. 133
5.14 Monitoring of HCl at position 9 during variation of the bubbler nitrogen flow rate .............................................. 133
5.15 Monitoring of HCl at position 3 during variation of the oxygen flow rate 134
5.16 Monitoring of HCl at position 5 during reactor start-up .............................................. 135
5.17 Monitoring of HCl at position 4 during reactor start-up .............................................. 135
5.18 The near infrared diode laser absorption system (NIR-LAS) and infrared grating spectrometer (IR-GAS) installed on the APCVD coating system .............................................. 136
5.19 Schematic of the IR-GAS and NIR-LAS setup on the coating system .............................. 137
5.20 Simultaneous monitoring with the IR-GAS and NIR-LAS system. The NIR-LAS system recorded HCl at two beams positions to the left and right of the inlet slot, the IR-GAS instrument MBTC in the reactor feed 138
5.21 Simulation of a complete blockage by stopping the flow through the bubbler. The NIR-LAS instrument measured HCl, the IR-GAS instrument MBTC in the reactor feed .............................................. 139
5.22 Variation of the bubbler temperature monitored by the IR-GAS system and compared to the Clausius-Clapeyron equation .............................................. 140
6.1 Transmission spectra of the Fibre Photonics Ltd. PIR 900/1000 fibre in the mid-infrared (provided by Fibre Photonics Ltd.) .............................................. 143
6.2 Comparison of the in-situ absorption monitoring arrangement using a polycrystalline infrared fibre and a mirror periscope .............................................. 144
6.3 Comparison of spectra recorded at atmospheric temperature in air. Blue spectra: FTIR and periscope, red spectra: FTIR and fibre optic cable; 20 samples; 1 cm⁻¹ resolution; 50 cm open beam path .............................................. 145
6.4 Setup of the FTIR spectrometer for in-situ measurements in the gas phase. Gap height between reactor head and substrate 7 mm.

6.5 Typical spectra recorded at standard operating conditions with and without H₂O (see Figure B.1 for page size version).

6.6 Setup for the decomposition of MBTC at variable temperatures with FTIR monitoring.

6.7 Spectrum of MBTC, Bubbler temperature 100.9 °C, Gas temperature in measuring cell 149.3 °C, resolution 0.5 cm⁻¹ (see Figure B.2 for page size version).

6.8 Decomposition of MBTC over a temperature range of 274 to 600 °C (see Figure B.3 for page size version).

6.9 Absorption peak of MBTC in the fingerprint region decays as decomposition progresses.

6.10 Decomposition of MBTC at 600 °C. Monitoring temperature 174 °C. Simulated spectra are calculated with HITRAN data, all other spectra are from the PNNL database of standard spectra at 50 °C.

6.11 Decomposition of MBTC at 600 °C and summation of all identified decomposition species (see Figure B.4 for page size version).

6.12 Decomposition of MBTC with oxygen over a temperature range of 177 to 767 °C (see Figure B.5 for page size version).

6.13 Decomposition of MBTC with oxygen at 600 °C. Monitoring temperature 174 °C. Simulated spectra are calculated with HITRAN data, all other spectra are from the PNNL database of standard spectra at 50 °C.

6.14 Measured spectra of the thermal decomposition of MBTC and oxygen at 600 °C with overlayed summation spectrum of individually identified components (see Figure B.6 for page size version).

7.1 Schematic diagram of the suggested workflow for setting up a computational simulation for species deposition in Fluent.

7.2 APCVD reactor coating head. a) Top view, b) Side view. Dimensions in mm. Substrate position is illustrated through blue outline in the top view.

7.3 Side view of the reactor geometry. Symmetry planes in green, pressure outlets in red, pressure inlets in blue and general walls in yellow.

7.4 Top view of the reactor geometry.
List of Figures

7.5 Cell centroids (red) and cell interfaces (blue) of a two dimensional mesh. A central cell C is surrounded by neighbouring cells. Values calculated at centroid points are interpolated to calculate interface values. ................................................................. 171
7.6 Model zones and meshing process ................................................................. 172
7.7 Residuals of the initial 150 iteration steps. Momentum equation is solved first, followed by the energy equation and the chemical species 175
7.8 Molar concentration in kmol m\(^{-3}\) of the MBTC-water complex with overlayed numerical mesh ................................................................. 177
7.9 Molar concentration in kmol m\(^{-3}\) of the hydrogen chloride (HCl) with overlayed velocity vectors along the symmetry plane (magnified) 178
7.10 Laminar diffusion coefficients for each species computed by Fluent (Units: m\(^2\) s\(^{-1}\)) ................................................................. 179
7.11 Thermal diffusion coefficients for each species computed by Fluent (Units: kg m\(^{-1}\) s\(^{-1}\)) ................................................................. 181
7.12 Mixture properties, reaction rates and cell Reynolds number computed by Fluent ................................................................. 182
7.13 Qualitative comparison of simulated and experimentally found deposition profiles (not to scale) ................................................................. 183
7.14 Pathlines of velocity superimposed on the surface deposition profile 184
7.15 Measured concentration of HCl compared to predicted concentration 1 mm above the substrate ................................................................. 186

8.1 Comparison of a density functional theory estimated absorption infrared spectrum of MBTC to a FTIR spectrum of MBTC (normalized). DFT spectrum x-axis scaled to match C–H vibration peak at 2900 cm\(^{-1}\) 193

B.1 Typical FTIR spectra recorded \textit{in-situ} in the APCVD gas phase at standard operating conditions with and without H\(_2\)O ........................................ 215
B.2 Spectrum of MBTC, Bubbler temperature 100.9°C, Gas temperature in measuring cell 149.3°C, resolution 0.5 cm\(^{-1}\) ........................................ 216
B.3 Decomposition of MBTC over a temperature range of 274 to 600°C 217
B.4 Decomposition of MBTC at 600°C and summation of all identified decomposition species ................................................................. 218
B.5 Decomposition of MBTC with oxygen over a temperature range of 177 to 767°C ................................................................. 219
B.6 Measured spectra of the thermal decomposition of MBTC and oxygen at 600 °C with overlayed summation spectrum of individually identified components . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 220
# List of Tables

1.1 Summary of common CVD process types, application examples and range of process conditions .................................................. 24

2.1 Common transparent conductive oxides (TCOs), dopants and deposition techniques ........................................................................... 50

2.2 Tin precursors for the APCVD of tin oxide ........................................ 52

2.3 Deposition model of tin oxide from MBTC, oxygen and water ............ 54

2.4 Deposition model of tin oxide from DMTC and oxygen ..................... 59

3.1 Lineshape and FWHM functions for fitting to spectral data ................. 73

3.2 Summary of laser diode materials .................................................... 77

3.3 Original Norton-Beer apodization function coefficients ...................... 84

5.1 Variable coating parameters .......................................................... 137

7.1 Lennard-Jones parameters of species used in the simulations .............. 173
Acronyms and Symbols

Acronyms

ALD atomic layer deposition.
ALE atomic layer epitaxy.
APCVD atmospheric pressure chemical vapour deposition.
CAD computer aided design.
CCD charge-coupled device.
CFD computational fluid dynamics.
CVD chemical vapour deposition.
DMTC di-methyl di-chloride.
FACVD flame assisted chemical vapour deposition.
FSR free spectral range.
FTIR fourier transform infrared spectroscopy.
FWHM full width at half maximum.
HCl hydrogen chloride.
IR-GAS infrared grating absorption spectroscopy.
LASER light amplification by stimulated emission of radiation.
LPCVD low pressure chemical vapour deposition.
MBTC mono-butyl tin tri-chloride.
NIR-LAS near-infrared (diode) laser absorption spectroscopy.
PC personal computer.
PECVD plasma enhanced chemical vapour deposition.
PVD physical vapour deposition.
QWOT quarter wave optical thickness.
SEM scanning electron microscopy.
TCO transparent conductive oxide.
TDL tuneable diode laser.
TTC tin tetra chloride.
USB universal serial bus.
VCSEL vertical cavity surface emitting laser.
**Symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>Absorbance.</td>
</tr>
<tr>
<td>$\alpha(\lambda)$</td>
<td>Absorption coefficient.</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom.</td>
</tr>
<tr>
<td>$A_r$</td>
<td>Arrhenius pre-exponential factor.</td>
</tr>
<tr>
<td>$B$</td>
<td>Amplitude of lineshape function.</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Temperature exponent.</td>
</tr>
<tr>
<td>$B(\nu)$</td>
<td>Instrument-function corrected irradiance.</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Constant.</td>
</tr>
<tr>
<td>$C_j$</td>
<td>Molar concentration of species $j$.</td>
</tr>
<tr>
<td>$c$</td>
<td>Species concentration.</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Heat capacity.</td>
</tr>
<tr>
<td>$D_{ij}$</td>
<td>Diffusion coefficient of species pair $i,j$.</td>
</tr>
<tr>
<td>$\vec{d}_i$</td>
<td>Mass diffusion.</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Maximum mirror displacement.</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Optical path difference.</td>
</tr>
<tr>
<td>$D_T$</td>
<td>Thermal (Soret) diffusion coefficient.</td>
</tr>
<tr>
<td>$E$</td>
<td>Energy.</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy.</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Lennard-Jones characteristic energy.</td>
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<tr>
<td>$\epsilon$</td>
<td>Molar extinction coefficient.</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Rate exponent.</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Dynamic viscosity.</td>
</tr>
<tr>
<td>$eV$</td>
<td>Electron Volt.</td>
</tr>
<tr>
<td>$F$</td>
<td>Volume flow rate.</td>
</tr>
<tr>
<td>$f$</td>
<td>Degree of freedom.</td>
</tr>
<tr>
<td>$f_D$</td>
<td>Correction factor.</td>
</tr>
<tr>
<td>$FSR$</td>
<td>Free spectral range.</td>
</tr>
<tr>
<td>$g$</td>
<td>Gravitational acceleration.</td>
</tr>
<tr>
<td>$g(\nu)$</td>
<td>Lineshape function.</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Activity of species.</td>
</tr>
<tr>
<td>$GHz$</td>
<td>Giga-Hertz.</td>
</tr>
<tr>
<td>$H$</td>
<td>Molar enthalpy.</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck constant.</td>
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<tr>
<td>$H(\nu)$</td>
<td>Function of FTIR instrument dependent factors.</td>
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<tr>
<td>$I$</td>
<td>Unit tensor.</td>
</tr>
<tr>
<td>$I_x$</td>
<td>Light intensity.</td>
</tr>
<tr>
<td>$j$</td>
<td>Diffusive flux.</td>
</tr>
<tr>
<td>$j$</td>
<td>Molecular angular momentum.</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant.</td>
</tr>
<tr>
<td>$k_i$</td>
<td>Forward reaction rate of reaction $i$.</td>
</tr>
<tr>
<td>$L/l$</td>
<td>Length.</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength.</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Thermal conductivity.</td>
</tr>
<tr>
<td>$M$</td>
<td>Mass flow rate.</td>
</tr>
<tr>
<td>$M$</td>
<td>Molecular weight.</td>
</tr>
<tr>
<td>$n$</td>
<td>Molecular number density.</td>
</tr>
<tr>
<td>$n_{ref}$</td>
<td>Refractive index.</td>
</tr>
<tr>
<td>$N_a$</td>
<td>Avogadro constant.</td>
</tr>
<tr>
<td>$N_g$</td>
<td>Total number of grating lines.</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Wavenumber.</td>
</tr>
<tr>
<td>$o$</td>
<td>Refraction order.</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Diffusion collision integral.</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Frequency.</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure.</td>
</tr>
<tr>
<td>$P_g$</td>
<td>Grating resolution.</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Vibrational state.</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Lennard-Jones potential.</td>
</tr>
<tr>
<td>$\phi_G$</td>
<td>Grating blaze angle.</td>
</tr>
<tr>
<td>$R$</td>
<td>Ideal gas constant.</td>
</tr>
<tr>
<td>$R_k$</td>
<td>Reaction rate.</td>
</tr>
<tr>
<td>$r$</td>
<td>Length.</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number.</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density.</td>
</tr>
</tbody>
</table>
Symbols

\( R_i \) Net rate of production of species \( i \).

\( \dot{R}_{i,r} \) Arrhenius rate of species \( i \).

\( s \) separation of grating lines.

\( S_i \) Rate of addition of species \( i \).

\( S_n \) Number of slits in spectrometer.

\( S(T) \) Linestrength.

\( \sigma(\lambda) \) Absorption cross section.

\( \sigma \) Lennard-Jones characteristic length.

\( T \) Temperature.

\( T^* \) Dimensionless temperature.

\( u \) Velocity vector.

\( \vec{V} \) Diffusive velocity.

\( w \) Width parameter.

\( w_g \) Full width at half maximum of the Gaussian, Lorentzian or Voigt lineshape function \( g = G/L/V \).

\( X \) Mole fraction.

\( x \) Length.

\( \xi(T) \) Specific volume.

\( Y_i \) Component mass fraction.
Abstract

Diagnostics and modelling of atmospheric pressure chemical vapour deposition reactors

The University of Manchester • Martin Hehn • Doctor of Philosophy (PhD)
24th June 2014

In the manufacturing process of float glass often atmospheric pressure chemical vapour deposition (APCVD) reactors are integrated on-line for the deposition of functional thin solid films. Such functional films have applications in architectural glass, flat panel displays and solar cells. As glass moves downstream in the process, the thin film is deposited at temperatures between 500 to 700 °C. The high temperatures make it difficult to monitor the deposition process and thin film quality control is commonly done at the end of the line or at lower temperatures. A time delay therefore exists between the point of thin film deposition and subsequent quality control, which can lead to large quantities of defective product being produced before faults are detected.

It is therefore desirable to monitor in the APCVD reactor for rapid feedback of unexpected deviations from desired process conditions, reaction progress and fault detection.

High uniformity of film properties across the substrate are important, but APCVD reactors are often empirically designed and the detailed chemical reaction mechanism is unknown. This leads to inefficient gas flow patterns and precursor utilization as well as difficulties in the design of new reactors.

The APCVD deposition of tin oxide from the mono-butyl-tin tri-chloride (MBTC) is an example of such a process.

Optical monitoring instruments \textit{in-situ} and \textit{in-line} on the APCVD reactor provided rapid feedback about process stability and progress non-invasively. Near infrared diode laser absorption spectroscopy (NIR-LAS) monitored the concentration of the reaction species hydrogen chloride (HCl) \textit{in-situ} and spatially in the coating zone. A mid-infrared grating absorption spectrometer (IR-GAS) with novel pyro-electric array detector monitored the concentration of precursor entering the coating system simultaneously. In combination these instruments provide the means for rapid process feedback.

Fourier transform infrared absorption spectroscopy (FTIR) was used to investigate the unknown decomposition pathway of the precursor to find the yet unknown key tin radical that initiates film growth. Stable species forming during MBTC decomposition over a temperature range of 170 to 760 °C were investigated but the tin intermediate remains unknown.

Computational fluid dynamics (CFD) is routinely employed in research and industry for the numerical simulation of CVD processes in order to predict reactor flow patterns, deposition rates, chemical species distribution or temperature profiles. Two and three dimensional models with complex geometries and detailed reaction models exist.

A three dimensional computational fluid dynamics (CFD) model of the used APCVD reactor was built using the Fluent CFD software. The numerical simulation included a chemical model that predicted qualitatively the chemical species distribution of hydrogen chloride in the gas phase. This was confirmed through comparison with NIR-LAS results. Design shortcomings due to inefficient flow patterns were also identified.

In combination the optical tools developed provide the means for safe and efficient manufacturing of thin films in APCVD reactors. CFD simulations can be used to increase precursor utilization and film uniformity in the development of new reactor designs.
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The author

Martin Hehn was born in Stuttgart, Germany, grew up and went to school in Neuhausen auf den Fildern and Esslingen am Neckar where he received his university entrance diploma (Abitur).

He started his undergraduate degree in process engineering at Stuttgart university and later transferred to the Hochschule Furtwangen university where he graduated in environmental and process engineering (Diplom Ingenieur). Throughout his undergraduate degree the author did two industrial placements, the first in water treatment (Hager+Elsässer, Stuttgart, Germany) and the second in plastic welding (Bielomatic, New Hudson, USA). In his undergraduate thesis at ROTA Yokogawa (Wehr, Germany) he was first introduced to computational fluid dynamics through modelling the pressure loss in coriolis flow meters.

For his postgraduate degree the author joined the 'Advanced chemical engineering' master course at the university of Manchester where he graduated with his master thesis about computational fluid dynamic modelling of an atmospheric pressure chemical vapour deposition reactor.

With the interest awoken for the modelling of chemical vapour deposition processes, the author joined the research group of Dr. Philip Martin at the university of Manchester as a doctoral candidate. In his work he investigates chemical vapour deposition processes through numerical modelling and infrared spectroscopy with the aims to reduce costs in production and to improve the quality control of such processes. During his time as a doctoral candidate he gave talks at two EuroCVD conferences and one at the CPACT meeting.
1 Introduction

1.1 Thin solid films

The deposition of thin solid film coatings onto surfaces are important industrial processes with a wide variety of applications. Increasing the hardness of surfaces, corrosion-resistivity, anti-bacterial properties, semiconductor manufacturing and transparent conductive films are only a few of the many areas where thin film coatings are applied (Bunshah 2010). The term thin film commonly refers to solid layers deposited with a thickness ranging from 5 to 600 nm (Seshan 2012).

Such thin films are created from a wide range of chemical precursors and processes depending on the application. The two main groups of surface deposition techniques are those in which a chemical reaction occurs and those where solely physical effects are responsible for the thin film formation. In physical vapour deposition (PVD) processes a film is created through evaporation of the precursor chemical and subsequent condensation on the substrate surface. Sputtering and molecular beam epitaxy are two popular PVD techniques often used in semiconductor manufacturing (Bunshah 2010).

Thin films created through the chemical reaction of one or more precursors are called chemical vapour deposition (CVD) processes (see Figure 1.1). Volatile precursors are mixed below decomposition temperature prior of entering the reactor. Reagents are then transported from the bulk gas stream to the deposition zone and reactions in the gas phase produce growth initiating intermediate species and by-products. Intermediates diffuse through the boundary layer (a thin layer close to the deposition surface) to the growth surface where they adsorb. Chemical reactions on the surface lead to film deposition and further by-products formation. The by-products desorb from the surface and diffuse into the bulk gas stream (Jones et al. 1997; Choy 2003).

Besides this general description of a CVD process consisting of at least one gas phase and one surface reaction, CVD processes are divided into subgroups such as low and atmospheric pressure, plasma enhanced and flame assisted CVD, depending on the deposited film type (Table 1.1). For each process type mentioned, further subgroups exist for certain speciality applications (Choy 2003).
1.1 Thin solid films

Figure 1.1: Basic steps of a CVD process for thin film deposition from two precursors (based on (Jones et al. 1997, p. 31))

Table 1.1: Summary of common CVD process types, application examples and range of process conditions

<table>
<thead>
<tr>
<th>CVD process type</th>
<th>Application example</th>
<th>Operating pressure</th>
<th>Operating temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low pressure (LPCVD)</td>
<td>Silicon oxide¹, silicon nitride²</td>
<td>0.01 to 10 mbar</td>
<td>500 to 1000 °C</td>
</tr>
<tr>
<td>Atmospheric pressure (APCVD)</td>
<td>Tin oxide³, zinc oxide⁴</td>
<td>1 bar</td>
<td>350 to 1300 °C</td>
</tr>
<tr>
<td>Plasma enhanced (PECVD)</td>
<td>Silicon oxide⁵, silicon nitride⁶</td>
<td>0.1 to 1 bar</td>
<td>20 to 500 °C</td>
</tr>
<tr>
<td>Flame assisted (FACVD)</td>
<td>Silver-titanium oxide⁷, gold⁸, tungsten⁹, molybdenum¹⁰</td>
<td>1 bar</td>
<td>combustion gas dependent</td>
</tr>
</tbody>
</table>


CVD is often a complex chemical system and non-equilibrium process. The deposition process involves reactions in the gas phase and on the substrate surface as well as chemisorption and desorption from the surface. The kinetics in a CVD could ideally be described by all elementary reaction steps and competing reactions whereas the
1.1 Thin solid films

gas phase reactions are ideally described by their chemical formula and rate equation (Choy 2003, p. 76).

If the deposition rate is kinetically controlled, it depends on the precursor concentration in the system. In a low pressure, low temperature CVD system the reactions would occur slow because of the low temperature. At low pressure the boundary layer is thin and diffusion coefficients are large which would lead to a surplus of reactants on the surface (Pierson 1999).

In contrast, at higher pressure and temperature the deposition is controlled by the mass transport. The deposition then depends on the diffusion of reactants through a much thicker boundary layer and the diffusion of desorbed by-products that diffuse through the boundary layer back into the bulk gas stream. Homogeneous gas phase reactions will also occur in those conditions which leads to growth inhibiting particle formation in the gas phase, non-uniform film and poorly adherent films. In consequence the diffusion of reactants is much more difficult compared to low pressure systems. Higher temperatures also cause more rapid gas phase reactions and molecules adsorbing on the surface instantly react which makes the diffusion through the boundary layer the limiting factor for the deposition rate (Choy 2003; Pierson 1999).

In order to favour the surface reaction and reduce film growth inhibiting gas phase reactions, films are often deposited at low pressures (LPCVD). For this a substrate is placed into an evacuated reactor vessel. The sub-atmospheric pressure increases the uniformity of the film as diffusion is increased and gas dynamics play a lesser role. Further, LPCVD extends the operating range of the process in which the film growth rate is determined by the chemical reaction rate (kinetic region) and not by the mass transfer to the surface (Figure 1.2). LPCVD processes are used in the semiconductor industry for the deposition of films such as silicon oxide, silicon nitride, gallium arsenide and indium phosphide (Choy 2003).

The rate of mass transport to the surface is higher than the surface reaction rate at low pressure whereas at atmospheric pressure the mass mass transport is slower than the surface reaction. Many CVD, PECVD and atomic layer epitaxy (ALE) deposition reactions are operated in the surface kinetic controlled reaction regime. The reason is the abundance of reactants near the substrate which undergo slow chemical reactions with only small local variations in precursor concentration. This makes the deposition of uniform films possible.
Due to the rapid gas phase reactions in mass transport controlled systems (e.g. APCVD), non-uniform coatings are more likely to occur due to depletion of precursor. The advantage of these systems, however, are the much higher deposition rates. Uniformity of the films can be improved through translational or rotational movement of the substrate, multiple precursor inlets or through temperature profiles (Choy 2003, p. 79; Luo et al. 2004; McCurdy 1999).

\[ \text{Thin film growth rate} \rightarrow P \text{Diffusion control} \]

\[ \text{Kinetic control} \rightarrow 1000 T^{-1} / K \]

**Figure 1.2:** Schematic of the growth regime depending on temperature and pressure (Pak et al. 2001, p. 37)

Despite its many advantages regarding film properties, LPCVD has the major drawback of using vacuum equipment which is expensive to operate and high maintenance. The cost of vacuum equipment also makes it difficult to coat large area substrates in a cost-efficient manner (Carlsson 2010).

### 1.2 Tin oxide thin films

Tin oxide is an important thin film material. Deposited on architectural glass, it reflects infrared whilst transmitting the visible light and is used to control the
temperature in buildings. Tin oxide films can also be manufactured to be electrically conductive and transparent. Doped with Fluorine (SnO$_2$:F), the conductivity of tin oxide is further increased and the film is used to dissipate electrical charges on flat panel displays and as a front contact for solar cells (see Figure 1.3, A. M. B. v. Mol, Chae et al. (2006)).

For the application in solar cells, the transmission characteristics, morphology and conductivity of the tin oxide layer are utilized. The incident light passes through the glass substrate onto which a tin oxide layer is deposited. The rough surface structure of the crystalline tin oxide causes the transmitted light to reflect in multiple directions and consequently to take a longer path through the semiconductor layer where the incident light produces an electrical charge.

After the semiconductor another tin oxide layer and a metal back reflector further reflect light back into the semiconductor. This is referred to as light trapping effect. The effect of trapping light in the cell enhances the efficiency of solar cells. Due to its conductivity the top tin oxide layer below the glass substrate is used together with the metal back reflector as electrical contact for charge transport out of the solar cell (Müller et al. 2004).

![Figure 1.3: Principle structure of an amorphous silicon solar cell. The rough surface morphology of the tin oxide layers causes the incident light to be trapped in the solar cell(A. M. B. v. Mol, Chae et al. 2006)](image)

Because of the glass substrate size required for flat panel displays or solar cells, tin oxide is deposited in an APCVD process, often incorporated in the glass manufacturing as an integrated process step. In such a process only a few seconds are available to coat the glass uniformly with a tin oxide layer of the desired properties (Ruske et al. 2007; Allendorf, Houl et al. 2006; Fehlner 1997).
1.3 Coating of large area substrates

Large area substrates are preferably coated at atmospheric pressure (APCVD). APCVD processes usually operate at the mass transfer limit to rapidly coat large areas of substrate in an on-line process (A. M. B. v. Mol, Chae et al. 2006). For this precursors are injected in the coating zone below decomposition temperature and a heated substrate provides the thermal energy to initiate reaction. Solar panel production, architectural low emissivity windows or flat panel displays are examples of products were large substrate areas require coatings.

The operation at atmospheric pressure reduces operating cost and the operation at the mass transport limit reduces production time as film growth rate is maximized. This is especially important for industries operating in highly competitive markets such as the consumer electronics or solar cell industry (Buchanan et al. 1997).

Commonly impinging CVD reactors are used in on-line deposition processes. In those reactors the volatile precursors are mixed below decomposition temperature and then fed into the reactor coating head. In the head the flow is laminarized and distributed over the width of the coating head. A laminar flow pattern is important for uniformity of the film and uniform precursor distribution. The laminar gas mixture then flows down vertically through an inlet slot, impinges onto the moving substrate and is extracted outside the reaction zone. The reaction gases are actively extracted to either one or both sides of the inlet slot (see Figure 1.4, R. Gordon (1997)).

![Figure 1.4: Cross sections of two common types of on-line APCVD coating systems](image)

**Figure 1.4:** Cross sections of two common types of on-line APCVD coating systems
1.4 APCVD manufacturing of tin oxide

One important application of APCVD is the deposition of tin oxide (SnO$_2$) during glass production on a float glass line. Float glass lines melt silica sand, boron trioxide and alkali oxides in a furnace. The molten glass mass then flows onto a bath of molten tin. The molten tin is a perfectly flat surface and the glass is spread out to 2 to 4 m in width, forming a perfectly flat glass panel. The glass is then cooled in an annealing kiln to avoid breakage due to thermal stress. The deposition of a tin oxide thin film can be incorporated into the glass manufacturing at the point where the glass temperature is 600°C.

In the case of tin oxide, more than one precursor chemical exists. Tin oxide can be deposited from tin tetra chloride (TTC), tetra-methyl tin (TMT), di-methyl di-chloride (DMTC) and mono-butyl tin tri-chloride (MBTC) (Goshtagore 1978; van Mol 2003; A. M. B. v. Mol, Chae et al. 2006).

Some of these precursors require moderation through additives such as alcohols in order to minimize undesired gas phase reactions which can lead to powder formation and subsequent film contamination if opaque particles are deposited onto the transparent tin oxide layer (H. Yates et al. 2010). The industry is interested in the fastest possible growth rate to reduce production time for cost savings purposes and MBTC has become a popular precursor for tin oxide deposition because of the high growth rates achievable (Allendorf, Houl et al. 2006).

1.5 Challenges in APCVD processes

A common challenge for APCVD processes is the deposition of films of uniform thickness and material properties across the substrate (Choy 2003, p. 81). In the case of tin oxide, a high uniformity ensures an even charge distribution and an uniform light transmission. The uniformity depends on large parts on the reactor design and how uniform the precursor gas stream can be distributed across the large substrate area. In atmospheric pressure processes the flow dynamics of the precursor gas stream are more dominant compared to LPCVD processes which makes it challenging to maintain laminar gas flow patterns in the reactor (Carlsson 2010).

It is common practice in the CVD industry to empirically improve the reactor design and operation. The coating head design is a key factor in achieving films of...
uniform thickness and properties. Empirical design and prototyping is a slow process as many design parameters are unknown and solely rely on the experience of the designer(s). Once a coating head is built, modifications on the geometry are difficult and time-consuming (Exarhos et al. 2007).

For control of the deposition process, the substrate, coating head, feed line and precursor evaporation system are temperature controlled (Tsakalis et al. n.d.; Carman et al. 1994). Further, the mass/volume flow rates of the inlet gas streams are also controlled. An issue that remains is that the actual deposition process in the reaction zone of the reactor is generally not monitored because access is limited. In addition, the flow field in the reactor should not be disturbed by monitoring probes extending into the coating zone as this would cause the deposition of non-uniform films. In a thermal CVD process, such as the APCVD of tin oxide, it would also be challenging for sensors to withstand the thermal stress caused by the close proximity of the coating head to the heated substrate (600 °C) (Volkov et al. 2008).

For those reasons, film quality control is often done at a later point in the process at lower or atmospheric temperatures. This is insofar problematic as faults in the tin oxide layer deposition are detected much later in the process after potentially tons of substrate are already coated with imperfections. A partial blockage in the feed pipes of the coating head, for example, cannot be detected with control measures mentioned above as the temperatures and flow rates are still identical to errorless operation.

A further issue is the determination of exact precursor quantities entering the reaction system. The precursor is either delivered through a bubbler system or through an evaporator. Especially in bubbler systems it is known that the liquid fill level has an influence on the concentration of precursor to the system (William J. Curran 2006; Bour et al. 2008). Controlling the exact precursor quantity is however important to maintain consistent material properties throughout a production shift (8 h).

### 1.6 APCVD process monitoring and control

#### 1.6.1 Challenges in APCVD process monitoring

CVD reactors are built to maintain a laminar flow regime in order to coat uniformly. Santen et al. found that with turbulent flow the mixing of precursor gases is improved
and conditions remain uniform in a large part of the reactor (Santen et al. 2000). This however decreases the conversion efficiency of the precursor which increases the total gas volume required. For this reason laminar flow is often preferred (Carlsson 2010).

A consequence of the flow disturbance minimization is that access to the reactor coating head is kept limited with metal shields that extend almost to the substrate surface, leaving only a gap of a few millimetres between the substrate surface and the coating head. As mentioned earlier, due to those restrictions in combination with the high process temperature process monitoring is difficult.

As a result, instruments for process control are installed elsewhere in the system where process conditions are less harsh. Among others, optical techniques such as reflectivity measurements to determine film thickness, haze measurements or Raman spectroscopy are used at the cold end of the process (see section 2.5 for a review of these techniques). These techniques require a top-down view field onto the substrate and can therefore only be used at a point in the process where the substrate is accessible.

Figure 1.5 shows the schematic of a glass production line with thin film coating ability and indications of possible points for process monitoring. It is evident, that there exists a time delay between the point of thin film deposition and quality control through process monitoring. It is therefore desirable to reduce or eliminate this time delay by monitoring in-situ in the APCVD reactor coating zone to gain instant feedback of thin film deposition progress and reaction stability. In the context of in-situ optical monitoring on CVD reactors, reaction stability refers to process conditions (process temperatures, precursor concentrations, flow rates, substrate speed) for which it is known that the desired film quality is produced. Optical monitoring has then the ability to detect deviations from this setpoint if process conditions change unexpectedly.

In consequence, monitoring techniques have to be identified that allow such in-situ monitoring and are of non-invasive character if used directly in the reactor coating zone. Suitable monitoring techniques require the ability to measure key factors of the deposition process. Because there is no access to the coating head for techniques relying on a top-down view field, only monitoring techniques that are able to monitor the reactor gas phase through the gap between coating head and substrate are
suitable. The gap is narrow and commonly in the range of 1 to 3 mm (Martin et al. 2007; Davis and Pemble 1999; Shao et al. 2009).

**Figure 1.5**: Schematic of tin oxide deposition on a float glass line with comparison of a standard control feedback loop and a potential optical monitoring supported feedback loop with faster control response
1.6 APCVD process monitoring and control

1.6.2 Proposed methodology for APCVD process monitoring

Precursors for many CVD applications including tin oxide deposition as well as gaseous reaction products are known to be infrared active (Beshkov et al. 2003; T. Kaneko et al. 2005; Paluszkiewicz et al. 1993; Martin et al. 2007). Infrared active chemical species can be detected and quantified through infrared spectroscopy such as Fourier transform infrared absorption spectroscopy (FTIR) or near-infrared diode laser absorption spectroscopy (NIR-LAS).

Absorption spectroscopy is an optical technique where light emitting from the spectrometer passes through a gas volume in which molecules absorb specific wavelength of the emitted light. The resulting decay in light intensity is then detected by a detector. This means that instruments such as FTIR and NIR-LAS require an unobstructed light beams path (e.g. the gap between coating head and substrate) (Demtröder 2008; Griffiths et al. 2008).

In FTIR absorption spectroscopy a light source emits a broad range of wavelength in the mid-infrared region of light and species absorbing specific wavelength of this broad wavelength range are detected simultaneously. In near infrared diode laser absorption spectroscopy, on the other hand, the laser is coherent light source emitting a single wavelength of light. Molecules absorbing this specific wavelength can be detected selectively with high sensitivity and high speed (Banwell et al. 1994).

Because of their mid-infrared activity, FTIR spectroscopy can monitor the tin-chlorine based precursors and potentially the growth initiating (tin containing) compounds. This would make it the ideal monitoring technique for APCVD tin oxide deposition because the gaseous intermediates could be directly related to film properties such as film thickness (see Figure 1.1). The disadvantage of FTIR for continuous process monitoring is however that fast detectors with a wide wavelength range and high detectivity require cryogenic cooling. This is especially problematic due to the high process temperature which would require a constant re-filling of the detector as liquid nitrogen evaporates. During filling no measurements can be made as the detector requires a settling time to reach its full performance. Further, liquid nitrogen needs to be held in storage on site.

FITR absorption spectroscopy is nevertheless an interesting technique in the investigation of the precursor decomposition. Often the detailed chemical reaction mechanism is unknown. In the case of MBTC the (tin containing) intermediates
initiating the film growth have yet to be found. For other precursors, such as TTC, hydroxytin compounds (e.g. \( \text{CH}_3\text{Cl}_2\text{SnOH} \)) were proposed as key intermediates (A. M. B. v. Mol, Chae et al. 2006; Choy 2003). Finding these key intermediates could facilitate process control (T. Kaneko et al. 2005; Paluszkiewicz et al. 1993; van Mol 2003).

Because of the unknown growth initiating intermediates, an uncertainty arises as to which is a suitable monitoring species and how existing APCVD processes for tin oxide deposition can benefit from the proposed "in-situ" monitoring. Martin et al. showed that NIR-LAS instruments can monitor CVD reaction species in the gas phase (Martin et al. 2007). Common tin oxide deposition by-products such as hydrogen chloride (HCl), methane (\( \text{CH}_4 \)) or additives such as hydrofluoric acid (HF) present overtone vibrations in the near-infrared which makes them accessible for near-infrared diode laser absorption spectroscopy. Although these molecules do not directly participate in the film formation, their presence is connected to the deposition reaction mechanism. It is therefore possible that monitoring a reaction by-product is sufficient to evaluate process stability, progress and quality (Chae 2006).

A practical advantage of NIR-LAS instruments is that through the advances made by the telecommunications industry in recent years, many parts of a laser system such as the laser sources themselves, waveguide cables and lenses are widely available and robust enough for continuous process monitoring. Laser light can be coupled into fibre optic cables over long distances with little losses. This allows for the NIR-LAS instrument to be located outside of the CVD reactor in a safe environment whilst the laser light is delivered through fibre optics to a point close to the coating zone. Light of a laser can be focused to small diameters of well under \( 1\text{ mm} \) over a distance of several meters. This is ideal for monitoring across the width of an APCVD coating head and through the small gap between coating head and substrate (Träger 2011; Demtröder 2008).

As mentioned in the previous section, the delivery of exact precursor quantities to the coating head is important for film properties, but mostly just controlled by the means of temperature and pressure in the evaporation system (Bour et al. 2008; William J. Curran 2006). An additional level of process control could ensure the correct precursor delivery rate, as well as providing instant fault detection in cases of malfunction in the evaporation system.
1.7 Modelling of APCVD processes

FTIR absorption spectroscopy applied in-line in the reactor feed lines could monitor the precursor concentration. Because of the disadvantages of FTIR spectrometers in production environment mentioned above another technique would preferred. Infrared grating absorption spectrometers (IR-GAS) have the potential to be used in such applications. In a grating spectrometer, infrared light is directed through a sample cell and onto a grating which diffracts the infrared light into its wavelength. Traditionally a gating spectrometer then rotates the grating to direct light of different wavelength onto a stationary detector (Palmer et al. 2005; James et al. 1969). Novel array detector elements however allow to build grating spectrometers without moving parts and the light of different wavelength is detected simultaneously. Such instruments can be built with small a footprint, making it easier to integrate in existing reactor systems. The spectral range is not as large as those of FTIR spectrometers, but sufficient to monitor selected spectral features of the precursor molecule (Ji et al. 2004; Richardson et al. 1990).

1.7 Modelling of APCVD processes

In section 1.5 it was mentioned that reactors in the CVD industry are often empirically designed. Because this is a slow process requiring prototyping of different reactor design modifications it appears advantage to be able to model the APCVD deposition process and to include the knowledge gained from process modelling into the reactor design.

The fluid dynamics chemistry of CVD processes are modelled since the 1970s, whereas low pressure processes were the main focus (Wahl 1977; Jensen 1987). At first modelling equations were solved analytically, but with increasing computational power more complex reaction schemes, multicomponent diffusion and entrance phenomena were modelled. Finite difference and finite and finite element solutions were introduced in the 1980s (Jensen 1987). Commercial fluid dynamic software packages soon started to incorporate CVD modelling because of the increasing interest of researchers and industry (Ulacia F. et al. 1989). Three dimensional models gained interest to investigate asymmetric effects in reactors and effects of reactor design changes (Roksnoer 1989; C. R. Kleijn and Hoogendoorn 1991; C. R. Kleijn 2000). With increasing importance in depositing films at atmospheric pressure, computational models of APCVD reactors became of interest. In recent years
Computational fluid dynamics (CFD) allows for the simulation of gas flow, heat transfer, chemical reaction, chemical species distribution and surface deposition. CFD is a numerical simulation method based on theoretical and semi-empirical equations. In the design stage of an APCVD reactor the proposed design can be modelled first to analyse the gas flow patterns in the coating zone. For this, the reactor geometry is modelled in a computer aided design (CAD) software and then imported in the simulation software. To model general flow dynamics, it might be sufficient modelling the reactor only with the carrier gas (e.g. nitrogen) but to predict the film growth rate or chemical species distribution, a chemical model is required (Wendt 2009; Fluent Inc. 2009).

The chemical model should ideally contain all elementary reaction steps including rate constants of these reactions. For the example of tin oxide deposition from MBTC those elementary reaction steps are however unknown. A simplified reaction model was created by Chae, Houf, McDaniel and Allendorf for the use in simulations. This chemical model only consists of two reaction steps, one in the gas phase and the second on the surface. This model is validated against experimentally measured growth rates with rate constants derived from low pressure experiments. It is unclear if the model also predicts gas phase species concentrations correctly or if the model is oversimplified in that respect. Being able to predict chemical species distribution in the reactor gas phase would allow to predetermine ideal optical monitoring position of either a new or existing reactor design prior to installation of the modelling equipment.

1.8 The thin film coating techniques and market

1.8.1 CVD in comparison to other thin film technologies

Besides CVD there exist a number of other technologies to deposit thin films onto surfaces. One of the main competitors of CVD is the afore mentioned physical vapour deposition (PVD). Aside from vapour based processes, there are wet and semi-molten processes such as slip casting, tape casting, calendering, screen printing
and plasma/thermal spraying. Wet chemical routes are mostly appropriate for thick coatings at a small scale because through the removal of binders and plasticisers in further sintering process steps such films present considerable shrinkage. Sol-gel films are known to crack easily and the layer thickness is limited to about 1 \( \mu m \) per coating layer and therefore require multiple coating passes. Plasma and thermal spraying processes often produce thick porous films (Choy 2003, p. 157).

Thin, highly pure and structurally controlled films, as required in the microelectric and opto-electronic industry, can only be manufactured with vapour based techniques. PVD has some disadvantages in comparison to CVD

- difficulty to deposit conformal films onto complex shapes as it is a line-of-sight process.
- expensive for large area coatings because of the need for a vacuum reactor
- difficulty to control the stoichiometry of films, which then influences film properties.

On the other hand, in PVD there are no chemical reactions, whereas CVD usually involves complex chemical gas phase and surface reaction mechanisms. The advantage of CVD is the ability to deposit films with desired properties at nanometre scale. Especially CVD at atmospheric pressure has the potential to be used at large scale (Choy 2003, p. 159 ff.).

1.8.2 Thin film market

The deposition of thin films especially with CVD processes is a multi-billion pound industry. Because of the wide spread use of CVD, this involves several industries:

**Coated structural glass** Large quantities of coated glass are used in architecture for environmental control in modern buildings by filtering UV- and reflecting IR-light. With appropriate coatings such as titanium oxide (self-cleaning properties) the functional area can be expanded even further. These films are deposited on large area glass substrates and the coating process is often integrated in a float glass line. In 2009 the value of finished products was estimated to 6.3 billion GBP (Ritala et al. 2009, p. 572).
1.8 The thin film coating techniques and market

**Silicon semiconductors** The largest market for CVD is the manufacturing of integrated circuits which are used in modern mobile devices, computers and electronic appliances. In 2009 the market was estimated to be 122 billion GBP with an additional 22 billion GBP for the speciality chemistry industry associated with semiconductor manufacturing. A challenge for the industry is the steadily increasing wafer size and decreasing feature size. The most important CVD technologies is epitaxy (the growth of layers with identical crystal structure as the wafer) (Ritala et al. 2009, p. 573).

**LEDs and opto-electronics** The manufacturing of LEDs has seen tremendous growth in recent years. Most mobile devices use LED backlights and car manufacturers have started implementing LED lighting. Further, through political decisions such as the phasing out of incandescent light bulbs the interest in LEDs is increased further (European Union 2008). Another, but significantly smaller market is the manufacturing of semiconductor lasers and optical detectors (Ritala et al. 2009).

**Solar cells** The market is estimated to grow to $8.3 billion by 2030 (Bunshah 2010). By 2008 the total photovoltaic capacity installed in the world was around 16 GW, in 2013 this has risen to 138.9 GW already, whereas 81.49 GW are installed in the European Union. Due to the political decision to reduce the subsidies for photovoltaic in countries such as Germany and Italy, less capacities were installed in recent years.

There exist a number of possible scenarios on how the solar market will develop in the EU until 2018. The European photovoltaic industry association (EPIA) has published several predictions on market development (see Figure 1.6) but there exists a large uncertainty because of the dependency on political decisions (EPIA 2012).

Outside the EU the biggest growth in photovoltaic capacity was observed in China, Japan and the USA, whereas China exceeds the growth of the latter two nations (EPIA 2012).

On the technical side, new solar cell performance records are reported frequently. The most promising technology for higher solar cell efficiency are multijunction cells. These cells consist of several semiconductor layers which allows the utilization of a wider wavelength range of light. Efficiencies of heterojunction cells in research are as high as 44.4%, but mass produced solar cells are often amorphous silicon cells with an efficiency of 13.4% or less (see Figure 1.7).
Figure 1.6: European Union photovoltaic capacity market development (data from EPIA (2012))
The thin film coating techniques and market

**Figure 1.7:** Development of solar cell efficiencies 1976 – 2014. Figure from NREL (National renewable energy laboratory, U.S. Department of Energy)
1.9 Summary

The deposition of thin solid films is important for a number of industries. Applications are the manufacturing of semiconductors, flat panel displays, architectural glass and solar cells. Depending on the application different techniques exist to deposit thin films whereas chemical vapour deposition (CVD) is the dominant manufacturing method. In CVD a minimum of two volatile precursors is used, whereas one of the precursors contains the key molecule or atom which is the key species for the deposited thin film. Through thermal or other energy the precursor is decomposed and forms intermediates containing the key tin-containing species. The intermediates then diffuses onto the surface where they reacts with the second precursor to a solid film and gaseous by-products. These reactions mechanisms are often complex with a number of gas and surface reactions some of which may inhibit the film growth.

In CVD reactors it is attempted to maintain a laminar flow pattern in order to coat the substrate uniformly over. Gas dynamics are less dominant in vacuum and some processes, especially in the semiconductor industry, requiring high uniformities use low pressure CVD (LPCVD). For applications using large substrates such as the coating of flat panel display glass or solar cells with tin oxide, atmospheric pressure CVD (APCVD) is used because vacuum equipment is costly for substrates of 3 to 5 m in width. The tin oxide deposition is often integrated into the on-line glass production where only a short period of time (in the order of seconds) is available to coat the substrate with a film of about 500 nm thickness.

The quality of the deposited film in an APCVD process depends on a number of factors such as deposition temperature, precursor concentrations and gas flow patterns. The precursor gas mixture entering the reactor has to be distributed uniformly for the resulting thin films to be uniform. The coating reactor therefore has to maintain a laminar flow field throughout the chemical reaction zone. The design of a coating head is hence one of the key factors in depositing uniform films of consistent properties.

Because it is crucial to maintain the laminar flow pattern in the reactor it is shielded well from the surrounding atmosphere, leaving only a narrow gap of 1 to 3 mm between the coating head and the glass substrate. Consequently it is difficult to monitor the deposition process. Further, the high process temperatures of 600 °C is a further challenge in monitoring the deposition process directly.
Conventionally film quality is controlled at a colder part of the process. This imposes a time delay between the point of thin film deposition and process monitoring. As a consequence, if a fault in the coating reactor occurs, defective product is produced for a time up to 30 min (depending on the line speed) before the error is detected. Common problems are impurities in the precursor building up overtime and partially blocking the precursor flow in some parts of the coating head.

It is therefore desirable to develop monitoring equipment with the ability to monitor in-situ in the reactor gas phase for instantaneous feedback of thin film deposition quality. Such monitoring tools would avoid the production of large quantities of defective products through early detection of problems and hence save cost in the production.

Suitable techniques for in-situ monitoring are Fourier transform infrared absorption (FTIR) and near-infrared diode laser absorption spectroscopy (NIR-LAS). Both instruments are non-invasive and have the ability to monitor the concentration and distribution of chemical species in the reactor gas phase. Due to some technical limitations, FTIR spectroscopy is less suitable for continuous process monitoring, but is applicable for the investigation of the often unknown chemical reaction mechanism in CVD processes. FTIR spectroscopy records spectra in the mid-infrared region of light where precursors and other reaction species often absorb. NIR-LAS instruments are highly selective, sensitive and fast in detecting some of the reaction species and are technically better suited for continuous in-situ process monitoring.

For further improvement of the process stability it is also suggested to monitor the quantity of the precursor containing the growth initiating molecule in-line in the reactor feed. Infrared grating absorption spectrometers (IR-GAS) with novel array detectors have the ability to monitor selected features of the mid-infrared light absorbing precursor molecules. Compared to FTIR spectrometers their spectral range is limited, but the instruments are of much smaller size and require no moving parts. It is further sufficient to only monitor a selected spectral feature of a precursor to quantify it.

For the development of new reactor designs and efficiency improvement of existing coating heads in regard to precursor distribution and utilization, computational fluid dynamics (CFD) is of interest. CFD has the ability to predict and visualize flow patterns in based on real reactor geometries. A chemical model can be added to the simulation to predict the chemical species distribution in the reactor gas phase and
growth rates on the surface. For the tin oxide deposition from MBTC the proposed model is a simplified reaction mechanism because elementary reaction steps are unknown. The model was validated with experimentally determined growth rates in a low pressure experiment. It is not clear if the model can predict chemical species distributions quantitatively and therefore validation with optical monitoring results is essential. If the model matches the experiment, simulations can be used to identify ideal monitoring positions in future reactor designs.

Chapter 2 reviews the literature relevant to the topic and chapter 3 introduces the specific methodology and fundamentals of the experimental tools used. A detailed description of experimental setups is then given in chapter 4.

Chapter 5 presents the findings targeted towards enhanced control of the APCVD reactor system, whereas chapter 6 addresses the understanding of the process. Chapter 7 then introduces modelling of an APCVD process depositing tin oxide.

The findings are then summarized and discussed in chapter 8 and conclusions are drawn. Section 8.2 highlights possible future work in the field.

1.10 Aims of this thesis

It is the aim of this thesis to gain process understanding and to provide control tools for large area substrates APCVD reactors. The intention is to improve the quality of thin films with specific properties and to provide means for a sustainable, safe and efficient manufacturing process. In addition the objective is to develop reactor design tools to facilitate the design of APCVD reactors.
2 Literature review

2.1 Introduction

Techniques and precursor chemicals to deposit thin films are known since a long time. A good review briefly summarizing the early developments of CVD can be found in (Ritala et al. 2009, p. 2–4).

Early work focused on different precursor chemicals, precursor combinations and operating conditions. The main emphasis in those works was the empirical determination of optimal precursor combinations and operation conditions to achieve desired film properties, mainly for the application in the semiconductor industry (Kane et al. 1975; Jarzebski et al. 1976; Rosler 1977; Muranori et al. 1978).

With the development of low-emissivity windows, flat panel displays and particularly solar cell panels, transparent conductive oxides (TCOs) gained much interest (Goetzberger et al. 2003; Chopra et al. 1983; Granqvist 2007).

Generally more than one precursor exists from which a certain type TCO can be deposited. In the development of precursor chemicals the focus is on high deposition rates and at the same time reduction or elimination of unwanted by-products formation which may contaminate the film (Ritala et al. 2009, p. 11–17).

TCO deposition on glass substrates is often integrated in the glass manufacturing process. Controlling the deposition process for reliable and repeatable product quality is of great interest for the glass manufacturers. For this, a range of (mostly optical) techniques was developed for process monitoring on the surface and in the gas phase of the deposition reaction. Incorporating monitoring instruments developed in laboratory scale to production is often difficult as they need to be integrated in the process and spatial as well as temperature constraints exist in such large scale processes. Nevertheless optical monitoring is of great importance for the CVD industry as a quality control tool (Herman 1996; Volkov et al. 2008; William J. Curran 2006).

Besides process monitoring, advances in the simulation and modelling of CVD processes has been made. Computational fluid dynamic simulations are frequently used to predict flow patterns in the reactor alongside with film growth rates and
2.2 Chemical vapour deposition

Chemical vapour deposition generally describes the process of depositing functional thin solid films from gaseous precursors onto substrates. A mix of precursor gases is flown into a reactor where they undergo reactions in the gas phase and on the surface of the substrate. The thin film is commonly deposited on heated substrates (e.g., glass) which provide thermal energy to the system (Ritala et al. 2009).

2.2.1 Principles of chemical vapour deposition

The thermal energy decomposes the precursor in the gas phase and the intermediate species formed initiate deposition on the surface. By-products are created and exhausted from the reactor along with excess precursor chemicals. These by-products are often gaseous but can be solids (powders) as well (Szanyi 2002; Major et al. 1983).

Jones et al. describe the CVD as a six step process (Jones et al. 1997):

1. The precursors are evaporated and mixed prior to entering the CVD reactor
2. Decomposition and reactive intermediates formation in the reaction and by-product formation

Because this work describes an approach to optimize the control and operation of a tin oxide deposition process using multiple techniques, this review first describes the fundamental concepts of CVD, CVD techniques and especially the production of tin oxide coatings in an APCVD process.

Following this, optical process monitoring and investigation tools and their application for process monitoring of a tin oxide deposition process are reviewed. Finally this review gives an overview over computational approaches to simulate CVD processes with a focus on tin oxide deposition.
2.2 Chemical vapour deposition

3. Mass transfer of the reactants to the substrate surface
4. Adsorption of the reactants on the surface
5. Diffusion on the surface to growth sites, nucleation and surface reaction leading to film formation
6. desorption of remaining chemical compounds and by products and mass transport in the bulk gas stream

In a thermally initiated CVD process three growth controlling regimes can be found. At lower temperatures (>500°C) the growth of thin film is determined by a rate limiting reaction step and increasing the temperature results in an exponential increase in the growth rate. This complies with Arrhenius's law

\[ R_k = A \exp \left( \frac{-E_a}{RT} \right) \]  (2.1)

where \( A_r \) is the pre-exponential factor, \( E_a \) the activation energy, \( R \) the gas constant and \( T \) the process/ deposition temperature. The activation energy is the slope of the plot of logarithmic growth rate over reciprocal temperature (see Figure 2.1, Pierson (1999)).

Towards higher temperatures (500 to 700°C) the growth rate rapidly increases to a point where the activation energy starts decreasing. This is an indicator that the film growth is no longer kinetically controlled. Instead the growth is limited by the mass transport of the precursor intermediates from the bulk gas through a boundary layer onto the surface. A weaker dependency to temperature can be found in this region.

At even higher temperature > 700°C secondary reactions in the gas phase and desorption from the surface occurs and the growth rate drops due to depletion of precursor in the gas phase (Choy 2003).

In atmospheric pressure CVD (APCVD) the mass transport limit is usually the limiting factor as the diffusion to the surface is much slower than the surface reaction. In low pressure processes (LPCVD) the mass transport is much faster than the surface reaction due to the reduced pressure. LPCVD is therefore often preferred as the uniformity of the film can be controlled much better in the kinetic growth region (Choy 2003, p. 77).
2.2 Chemical vapour deposition

Thermal control
Diffusion control
Kinetic control

\[
\begin{align*}
1000T^{-1} /K & \rightarrow \\
\text{Growth rate } & \rightarrow \\
\uparrow \text{Temperature /K} & \rightarrow
\end{align*}
\]

**Figure 2.1:** Growth rate (logarithmic) as a function of the growth temperature

Thin film deposition through CVD is a versatile technique and many different processes exist which use a wide range of chemical elements and reactor types. Pak et al. compiled a table of elements whose use in CVD applications has been reported (Pak et al. 2001). The table covers most elements of the periodic table but the most important materials are those used in the semiconductor industry. The III-VI group contains elements such as Silicon, Gallium, Arsenide, Indium and Tin. Further, (transition) metals such as Titanium, Vanadium, Silver and Zinc are in this group and oxides of these materials are deposited in CVD processes.

### 2.2.2 Chemical vapour deposition reactors

Depending on the chemistry involved, different CVD reactor types are used. Low pressure processes (LPCVD) require a vacuum process where the substrate is placed into the reactor, followed by extraction of the air and subsequent injection of the precursor chemicals (Figure 2.2). These types of reactors are frequently used in
2.2 Chemical vapour deposition

semiconductor manufacturing of e.g. gallium-arsenide or indium-phosphide films in rotating disc reactors. In this reactor type the precursors flow vertically down onto a rotating substrate and excess gases are extracted to the side of the substrate. The rotation of the disc as well as the vacuum enhances the uniformity of the film across the substrate (Figure 2.2a). The side walls of the reactor can be either heated (hot-wall reactor) or not (cold-wall reactor) [R. Gordon 1997; Pak et al. 2001, p 9–12.

![Figure 2.2: Rotating disc reactor with vertical impinging flow](image1)

![Figure 2.2: Horizontal tube reactor](image2)

(a) Rotating disc reactor with vertical impinging flow

(b) Horizontal tube reactor

Figure 2.2: Two common CVD reactor types for vacuum coatings. The horizontal tube reactor can be operated at atmospheric pressure as well

In horizontal tube reactors the substrate is processed similarly to LPCVD reactors. In this configuration the substrate is placed into a tube and precursor flows into one side of the reactor, across the substrate surface and to the exhaust on the opposed tube end. The tube is most commonly quartz and can be operated in hot- or cold-wall configuration. This type of reactor is often used in laboratory scale experiments and more recently in the deposition of graphene as well (Inagaki et al. 2014, ch. 3). Both, atmospheric (APCVD) or low pressure processing are possible (Figure 2.2b, Pierson (1999, ch. 5)).

High throughput reactors operating at atmospheric pressure are favoured in industrial applications such as the deposition of transparent oxides for coating of window glass, flat panel displays or solar cell panels. The advantage of atmospheric pressure processes is the lower cost compared to LPCVD and high processing speed. This is particularly important for the functional glass and solar cell industry where due to cost pressure large areas of substrate need to be coated within seconds and on-line.
APCVD is frequently applied in the production of low-emissivity glass and in the deposition of solar cell top layers made from fluorine doped tin oxide. In such online processes the glass floats on a bath of liquid tin and moves at a constant line speed. The coating head is positioned stationary above the float glass and the precursor flow impinges on the substrate. Exhaust gases are extracted to the sides of the reaction zone (Figure 2.3, A. M. B. v. Mol, Chae et al. (2006) and Granqvist (2007)). Other techniques such as Plasma Enhanced CVD (PECVD), Atomic Layer Deposition (ALD) are also frequently used and commonly use the introduced reactor geometries with small modifications (Bunshah 2010; Ritala et al. 2009; Johnson et al. 1983).

**Figure 2.3:** High throughput APCVD coater with moving substrate

### 2.3 Transparent conductive oxides

Transparent and conductive thin films (TCOs) are an important group of films for the solar cell and other industries. TCOs are used as front contacts in solar cells, in the manufacturing of architectural and automotive glass and flat panel displays (A. M. B. v. Mol, Chae et al. 2006; Müller et al. 2004).

A large number of transparent conductive oxides exists, whereas indium tin oxide, zinc oxide and tin oxide are the main materials used. Doping can increase the electrical conductivity of the film, although an inverse relationship to the film transparency exists which limits the amount of doping (see Table 2.1; Edwards et al. (2004)).
The application of TCOs as solar panel front contact is of particular interest. Although fluorine doped indium oxide films (Kiriakidis et al. 2009) and fluorine doped zinc oxide films (Hu and R. Gordon 1991) have been used in solar cells, fluorine doped tin oxide is the cheapest material and therefore often the choice of many solar cell manufacturers operating in highly competitive markets (R. Gordon 2000).

Table 2.1: Common transparent conductive oxides, dopants and deposition techniques (R. Gordon 2000)

<table>
<thead>
<tr>
<th>TCO</th>
<th>Dopant</th>
<th>Deposition technology</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium oxide In$_2$O$_3$</td>
<td>Sn</td>
<td>Aerosol CVD</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>Sputtering</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>Spray pyrolysis</td>
<td>3</td>
</tr>
<tr>
<td>Zinc oxide ZnO</td>
<td>Al</td>
<td>Sputtering</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>In</td>
<td>Spray pyrolysis/CVD</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>APCVD</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Ga</td>
<td>APCVD</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>APCVD</td>
<td>8</td>
</tr>
<tr>
<td>Tin oxide SnO$_2$</td>
<td>F</td>
<td>APCVD</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>Spray pyrolysis</td>
<td>10</td>
</tr>
</tbody>
</table>

1 (Maki et al. 2003)  
2 (Cho et al. 2008)  
3 (Kiriakidis et al. 2009)  
4 (Jiang et al. 2003)  
5 (Major et al. 1983)  
6 (Hu and R. Gordon 1993)  
7 (Hu and R. G. Gordon 1992)  
8 (Hu and R. Gordon 1991)  
9 (Sheel, H. M. Yates et al. 2009)  
10 (Proscia et al. 1992)  
11 (Rajpure et al. 2011)

In a solar cell the thin film TCOs serve multiple purposes:

- transmission of the visible light (A. M. B. v. Mol, Chae et al. 2006)
- electrical charge transport (Proscia et al. 1992)

Typically these thin films are deposited during glass manufacturing as an integrated process step. Industrially the focus is on cost efficient deposition at high speeds and on-line. For this it is desirable to deposit thin films at atmospheric pressure because
costs for APCVD are 2-2.5 times lower compared to LPCVD processes. Further, at lower pressures the growth rates are much slower and large vacuum equipment would be required to accommodate glass of 2 to 5 m in width (M. Li et al. 2006).

2.4 Chemical vapour deposition of tin oxide

As mentioned above, tin oxide is the most common front contact material used in single layer solar cells and large scale production of tin oxide (see section 1.2). The material has a number of favourable properties as a solar cell top layer:

- high transparency for the visible light (R. Gordon 2000)
- high conductivity (doping with fluorine) (Proscia et al. 1992; Subba Ramaiah et al. 2006)
- mechanical hardness (R. Gordon 2000)
- environmental stability (A. M. B. v. Mol, Chae et al. 2006)

In solar cells the tin oxide layer is depositioned in between the glass substrate and the semiconductor. Its purpose is the scattering of the incident light into the semiconductor and the reflection of any back-reflected light from the back reflector or the semiconductor (light-trapping). Therefore the morphology of the layer is of great importance. Thicker films usually lead to a more featured films with improved light scattering but the transparency is reduced (H. Yates et al. 2010). The electrical energy generated in the solar cell is transported through the conductive tin oxide layer to contacts on the side of the solar cell (A. M. B. v. Mol, Chae et al. 2006). Doping with e.g. fluorine increases the conductivity and lowers transport losses but the optical transmittance decreases inversely (H. Yates et al. 2010).

Tin oxide films are industrially mainly deposited from the precursors presented in Table 2.2, although a wide range of other possible organo-tin precursors exists (Lindner 1986).

TTC and TMT were used first for tin oxide in combination with oxygen or water vapour (Ghoshtagore 1978; Zawadski et al. 1992). Due to its high reactivity in the gas phase, TTC favours powder formation and only moderation of the reaction with alcohol showed desirable results (H. Yates et al. 2010).
In the subsequent precursor development, the four chlorine molecules of TTC were partially or completely replaced by alkyl molecules to stabilize the precursor molecule. DMTC and MBTC are two examples of precursors that contain alkyl groups as well as chlorine. The presence of alkyl groups strengthens the Sn–Cl bond which moderates the gas phase reactivity particularly at atmospheric pressure (S.-M. Lee et al. 2000). Lindner states that the preferred configuration of a tin precursor is R–SnX$_{4-a}$ with R being a C$_1$–C$_4$ alkyl group, X a halogen which is preferably chlorine and a is 1 or 2 (Lindner 1986).

**Table 2.2: Tin precursors for the APCVD of tin oxide**

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin tetra chloride (TTC)</td>
<td>SnCl$_4$</td>
<td>1</td>
</tr>
<tr>
<td>Tetra-methyl tin (TMT)</td>
<td>(CH$_3$)$_4$Sn</td>
<td>2</td>
</tr>
<tr>
<td>Di-methyl tin di-chloride (DMTC)</td>
<td>(CH$_3$)$_2$SnCl$_2$</td>
<td>3</td>
</tr>
<tr>
<td>Mono-butyl tin tri-chloride (MBTC)</td>
<td>C$_4$H$_9$SnCl$_3$</td>
<td>4</td>
</tr>
</tbody>
</table>

1 (Muranori et al. 1978) (Ghoshtagore 1978) (Goshtagore 1978) (Dakaldiran et al. 2009)
2 (Goshtagore 1978) (Borman et al. 1989) (Proscia et al. 1992)

In a production environment the deposition rate is regarded as one of the highest process priority. In this respect MBTC exceeds other precursors and therefore is the most commonly used tin oxide precursor to date. It was found that the high reaction rate in combination with oxygen can be further increased by the addition of water (Lindner 1986; Chae 2004; S.-M. Lee et al. 2000). Figure 2.4 shows growth rates over temperature for the DMTC and the MBTC precursor with oxygen and water addition. Precursor concentration is not identical for all plots but it can be seen that water addition has no effect for the DMTC precursor but the MBTC growth rate significantly increases with water addition (commonly around 1.5 mol%). Allendorf, Houl et al. speculate that the presence of water creates OH groups on the surface that more rapidly convert the tin intermediates (Allendorf, Houl et al. 2006).

Because of the importance of the MBTC precursor for industrial tin oxide deposition, Chae, Houf, McDaniel and Allendorf developed a kinetic model for the MBTC + O$_2$ and the more important MBTC + O$_2$ + H$_2$O system. Models are based on
2.4 Chemical vapour deposition of tin oxide

Figure 2.4: Comparison between DMTC and MBTC APCVD film growth rates. Refer to the references for process conditions.
is then achieved through modification of the pre-exponential factor. M. Li et al. found that when they used this mechanism in a computational model, the proposed pre-exponential factor of the surface reaction had to be reduced by several orders of magnitude (M. Li et al. 2006).

Further it has to be noted that the mechanism is solely matched to experimentally observed growth rates. By-products such as ethylene and hydrogen chloride are said to be created in a certain concentration ratio and to match the atomic quantities. This means that predicted gas phase quantities of species will not necessarily match experimental quantities. Davis, T. v. Mol et al. however employed a global two step mechanism for the reaction of DMTC + O₂ and found a good match of predicted and experimental values for the growth rate and the by-product methane alike (Davis, T. v. Mol et al. n.d.).

Quantitative measurements of gaseous by-products of the MBTC + O₂ + H₂O system at atmospheric pressure do not exist to date, therefore it is unclear if a two step model sufficiently describes this chemical reaction system.

### Table 2.3: Deposition model of tin oxide from MBTC, oxygen and water (Chae 2006)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>Eₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄H₉SnCl₃(g) + H₂O(g) → C₃H₉SnCl₃−H₂O(s)</td>
<td>4 × 10¹⁴</td>
<td>10 000</td>
</tr>
<tr>
<td>C₃H₉SnCl₃−H₂O(s) + ½ O₂ → SnO₂(B) + 2 C₂H₄(g) + 3 HCl(g) + OS(s)</td>
<td>1 × 10¹⁰</td>
<td>13 700</td>
</tr>
<tr>
<td></td>
<td>2.5 × 10²</td>
<td>(M. Li et al. 2006)</td>
</tr>
</tbody>
</table>

(g) denotes gaseous, (s) surface absorbed and (B) solid surface species  
ₐₐ (mol cm⁻² s⁻¹ K) is the pre-exponential factor, Eₐ the activation energy (cal mol⁻¹)  
and kᵢ the forward reaction rate of reaction i

### 2.4.1 Deposition temperature

The target of industrial tin oxide deposition is to achieve rapid growth rates. S.-M. Lee et al. reports that the reaction of MBTC with oxygen and water is kinetically controlled by a rate determining reaction step up to a temperature of around 560 °C (S.-M. Lee et al. 2000). Towards higher temperatures the reaction appears to be mass transport limited where the rate of deposition is only increased by an increase in precursor concentration. In the kinetically controlled region the deposition rate is lower compared to the mass transport limited region (Choy 2003). For this reason tin oxide deposition is carried out at 600 °C in industrial processes. At this
temperature the process is operated in the mass transport limited region and the glass substrate surface is sufficiently flat and hardened (Figure 2.5; Blocher (1981)). Further it is known that temperature variations across the substrate result in non-uniform films. This is an issue in thin film production as optical properties such as the transmission and reflectivity change with film thickness (McCurdy 1999; Or et al. 2002). It was shown that tight control of the substrate temperature results in improved uniformity of the deposited film (van Bilsenm et al. 2000).

![Figure 2.5: Temperature dependency of the growth rate for varied water content. MBTC concentration 1 mol%, oxygen to nitrogen ration: 0.2 (S.-M. Lee et al. 2000)](image)

2.5 Optical monitoring on chemical vapour deposition processes

Optical monitoring is employed on CVD processes for three reasons, investigation of film properties, fundamental investigations of the deposition reaction and on-
line process monitoring on the surface or in the gas phase for quality control in a manufacturing environment.

Various techniques exist for those different purposes. For the investigation of surface properties samples of thin films are processed off-line. Scanning electron microscopy (SEM) is used to characterize films through analysis of the morphology. X-ray diffraction is also often employed for the measurement of film thickness, density, roughness as well as crystal structure and orientation (H. Zhao, Q. Liu, Yang et al. 2008; H. Y. Lee et al. 2008; Aukkaravittayapun et al. 2006). Raman spectroscopy can also be used to identify film composition – off-line and on-line(Beshkov et al. 2003; Davis and Pemble 1999).

Besides direct surface investigations, other optical techniques exist to investigate CVD gas phase reactions. Paluszkiewicz et al. report monitoring results from the deposition of Si$_3$N$_4$ from SiH$_4$ and NH$_3$ using FTIR spectroscopy (Paluszkiewicz et al. 1993). With samples drawn from the gas phase they were able to conclude that oxygen as a contaminant inhibited their reaction. Beshkov et al. investigated the same reaction system using FTIR and Raman spectroscopy on atmospheric, low pressure and plasma enhanced CVD reactors (Beshkov et al. 2003). Davis and Pemble also employed Raman spectroscopy to monitor methane spatially in an APCVD reactor (Davis and Pemble 1999).

For the deposition of silicon-oxynitride fibres Vogt et al. used in-situ FTIR monitoring which allowed them to identify the growth initiating species (Vogt et al. 2000). T. Kaneko et al. monitored the Si–C, Si–H and C–H content of their PECVD reaction depositing SiC:H (T. Kaneko et al. 2005). A. M. B. v. Mol monitored the decomposition of DMTC in a low pressure continuously stirred tank reactor and identified decomposition products such as formaldehyde, methane, hydrogen chloride but not the key growth initiation tin compounds (van Mol 2003).

The limitations of FTIR spectroscopy is that only dipole containing molecules are detected and only in the mid-infrared region of light. Therefore single atom radicals or molecules such as hydrogen are not detected and neither are molecules that absorb light outside of the typical monitoring region of 500 to 4500 cm$^{-1}$ (Smith 2011).

On-line monitoring on float glass lines serves the purpose of quality control in the process. Monitoring techniques require the ability to monitor non-intrusively and at the high line speed. Depending on the position in the process, instruments must
also withstand high heat (> 600°C). A method to monitor film thickness in-situ was demonstrated by Rivero et al. (Rivero et al. 1999). The system is based on a light source and a detector detecting changes in reflectivity as the film grows. Their work illustrates well the challenges in optical CVD process monitoring (Figure 2.6). A FTIR spectrometer and a Raman spectrometer were used simultaneously and both instruments require a certain view field. The FTIR requires an infrared light beam to pass through the gap between sample and top plate whilst the Raman laser source and detector need a view field onto the surface.

Another thickness measuring technique was demonstrated by Volkov et al. although their instrument is a commercial product and little information is given about the experimental setup (Volkov et al. 2008).

A further approach to process control was presented by Martin et al. (Martin et al. 2007). They monitored chemical species concentrations directly in the reactor gas phase using near infrared diode laser absorption spectroscopy. Their work aimed to provide information about the reaction stability (see subsection 1.6.1) in-situ in an APCVD reactor depositing tin oxide from a tin tetra-chloride precursor. The concept was successfully demonstrated by using hydrogen chloride and hydrogen fluoride as monitoring species. Limited access to the reactor allowed monitoring at only two positions on a roll-to-roll process. The work highlights, that it is crucial to

![Figure 2.6: Setup to measure in-situ film thickness and gas phase composition by (Rivero et al. 1999)](image-url)
2.6 The application of computational fluid dynamics for chemical vapour deposition

find optimal monitoring positions in order to detect changes in the deposition with sufficient detail (Figure 2.7). At the first monitoring position, changes to the process were detected which were much more subtle compared to the second position. The reason for this is the reactor geometry, gas flow patterns and the chemistry involved. Their first monitoring point was close to the chemistry inlet where reaction products such as HCl are quickly displaced whereas the second monitoring point is further in the reaction zone where the precursor decomposition has progressed further and hence the by-products concentration is higher.

![Figure 2.7](image)  
**Figure 2.7**: Concentration of HCl monitored at two points on an roll-to-roll APCVD process with laser absorption spectroscopy during variations of process conditions (Martin et al. 2007)

2.6 The application of computational fluid dynamics for chemical vapour deposition

Although the general equations to compute fluid dynamics have been known for a long time (Batchelor 1967), the first simulations of CVD reactors are found in the 1970s. These early models used analytical solutions for two dimensional flows with mass transfer controlled deposition rate. Beginning with the 1980s, more complex models emerged because of the increase in computational power. Detailed reaction kinetics,
multicomponent diffusion, surface deposition and boundary layers were computed numerically with finite difference and finite element methods (Wahl 1977; Coltrin 1984; Jensen 1987; Ern et al. 1997; C. R. Kleijn 2000). Commercial CFD software packages started implementing CVD capabilities due to the fact that modelling of CVD processes had gained interest in industry and from researchers (Ulacia F. et al. 1989). Since it was known that the reactor design has major impact on film uniformity and film property homogeneity, three dimensional modelling became increasingly important. 3D modelling also allows the analysis of asymmetric effects as they are observed in real deposition reactors (Roksnoer 1989; C. R. Kleijn and Hoogendoorn 1991; C. R. Kleijn 2000).

Santen et al. investigated a rotating disc CVD reactor used in semiconductor industry e.g. for the deposition of gallium-arsenide and noted that for larger areas the generally made assumption of laminar flow in the reactor may not hold (Santen et al. 2000). For the same reactor type Luo et al. computed the flow patterns of different geometry modification in order to find the optimal geometry for deposition on large area wafers (Luo et al. 2004). It was found that the uniformity of the film can be greatly improved by guiding the precursor gases and elimination of dead volume in the reactor (Luo et al. 2004).

For tin oxide deposition from DMTC a model was developed to predict the growth rate in a horizontal flow tubular APCVD reactor (van Mol 2003). The model uses a global two step chemical pathway consisting of a gas phase and a surface reaction (Table 2.4). Gaseous by-products are produced in quantities to match the overall atomic balance in relation to the growth initiating intermediate \( \text{CH}_3\text{SnCl}_2\text{OH} \). The gas phase reaction rate is selected to be much faster than the surface reaction rate which controls the deposition rate.

### Table 2.4: Deposition model of tin oxide from DMTC and oxygen (van Mol 2003)

| Gas phase | \((\text{CH}_3)_2\text{SnCl}_2(g) + \text{O}_2(g) \xrightarrow{k_1} \text{CH}_3\text{SnCl}_2\text{OH} + \frac{1}{2} \text{CO}_2 + \frac{1}{4} \text{CH}_4\) |
| Surface | \((\text{CH}_3\text{SnCl}_2\text{OH}(s) + \text{O}_2(s) \xrightarrow{k_2} \text{SnO}_2(B) + 2\text{HCl(g)} + \text{CH}_2\text{O})\) |

\((g)\) denotes gaseous, \((s)\) surface absorbed and \((B)\) solid surface species

It was found that the model can predict the growth rate distribution accurately with little growth on the reactor inlet and the highest growth rate at the reactor outlet where the temperature of the gases is highest. The model was expanded for
validation with laser absorption monitoring results of methane. It was shown that the simplified chemical reaction mechanism used in the simulation can predict also gas phase chemical species distributions (Hehn 2009).

M. Li et al. presented a two dimensional model of an on-line dual flow APCVD coating system with impinging flow for tin oxide deposition from MBTC (M. Li et al. 2006). In this work the effect of a moving substrate was evaluated for different substrate speeds of up to $2 \text{ m s}^{-1}$. It was found that at high speeds the downstream deposition rate is much higher compared to a stagnant flow profile due to an altered velocity profile. It appears that the rapidly translating substrate favours a flow of chemicals in the downstream direction.

Similarly to the chemical model used by A. M. B. v. Mol previously, a two step reaction mechanism was proposed by Chae, Houf, McDaniel and Allendorf for the reaction of MBTC with water and oxygen (see Table 2.3) (van Mol 2003; Chae 2006). It was found that the surface reaction step, which controls the deposition rate, required adjustment in order to match experimental film thickness measurements. In the original mechanism the reaction rate at the point where the flow impinges on the substrate was largely over predicted. A slower surface reaction rate gave a good fit to the experimental data (Figure 2.8). The large difference between the original mechanism to the adjusted mechanism indicates that a growth inhibiting reaction occurring in the gas phase of the inlet is not accounted for by this global mechanism (M. Li et al. 2006).
2.6 The application of computational fluid dynamics for chemical vapour deposition

Figure 2.8: Comparison of experimental data to the original model mechanism and the surface reaction rate adjusted mechanism. Data from: (M. Li et al. 2006). \(x/B\) is a length from the impinging flow to the extraction.
3 Methodology

3.1 Introduction

For the analysis and control of CVD processes a range of monitoring equipment is used. Some techniques are based on the analysis of properties of the surface of the deposited thin film, others analyse the composition of the gaseous precursor mixture which precedes the thin film deposition.

It was highlighted in chapter 2 that the use of surface and gas phase monitoring techniques for CVD processes is reported. It became evident that the monitoring of thin film surface properties is done in the cold part of the glass manufacturing process whereas the thin film is actually deposited at high temperatures. This leads to a time delay between the deposition process and the analysis of film quality (see Figure 1.5).

In the endeavour to provide the means for a more instantaneous feedback of the thin film deposition process, optical monitoring was identified as a suitable bundle of techniques to overcome the problem of time delayed feedback in the manufacturing process. Some optical monitoring techniques can be used in-situ in the reactor gas phase.

In the analysis and monitoring of gaseous precursors a variety of techniques exist that allow the identification and quantification of such molecules. It is important to understand which method of monitoring is applicable for a certain molecule type in order to make a decision as to which technique can be applied. Furthermore the selected technique and therewith the instrument used, must be able to function reliably in the environment of the process. Structural limitations as well as the high process temperature should ideally not influence the precision of the instrument or its long term functionality.

In the following, the fundamental principles of spectroscopy are provided. Based on these fundamentals, reasoning as to why a certain technique was selected in this work is provided. Later in the chapter details of the methodology namely near-infrared absorption spectroscopy and Fourier transform infrared absorption spectroscopy are provided.
3.2 Fundamentals of spectroscopy

3.2.1 The electromagnetic spectrum

In spectroscopy the response of substances to electromagnetic radiation is recorded in a spectrum. The electromagnetic spectrum stretches from wavelength beyond the atomic level to wavelength of metres or even kilometres. The spectrum includes the comparable small region of visible light as well as the shorter ultraviolet waves and the longer infrared waves. Electromagnetic radiation can be considered as energy (photons) with wave or particle-like behaviour. Figure 3.1 shows the electromagnetic spectrum. For radiation with the frequency $\omega$ the photons have a discrete energy level $E$, which can be calculated using the Planck equation

$$E = h \cdot \omega$$

(3.1)

where $h$ is the Planck constant (Hollas 2002). Just like the energy of radiation is quantized, so are atoms and molecules. This means that their energy can only have specific quantized values. Based on their interaction with an external magnetic field, rotational, vibrational, electronic and further levels can be distinguished in molecular systems.

Electrons in molecular systems can jump between energy levels if stimulated by external electromagnetic radiation (photons), which can lead to the phenomena of stimulated absorption, stimulated emission and spontaneous emission. Stimulated absorption is important in the industrial gas analysis. A molecular system which is exposed to electromagnetic radiation of frequency $\omega$ absorbs an energy quantity of $h \cdot \omega$ from the photon. A consequence of this absorption is a change of energy level of the molecular system. The molecule is raised from its current energy state to a higher level. This stimulation only occurs, however, if the photon energy matches the energy separation of the two quantum energy states. Because the nuclei of a molecule are much heavier compared to the electrons in the molecule, it can be shown that the wave function can be factorized into electron and nuclei contributions. The molecule itself rotates and vibrates and hence the nuclei contribution can be further
3.2 Fundamentals of spectroscopy

Figure 3.1: The electromagnetic spectrum (based on (Hollas 2002))

separated into vibrational and rotational contributions. It can be said that the total energy of a molecule is the sum of electronic, vibrational, translational, rotational and kinetic energy (Hollas 2002; Banwell et al. 1994).

\[ E_{\text{total}} = E_e + E_v + E_t + E_r + E_k \]  \hspace{1cm} (3.2)

The grouping of spectroscopy into vibrational or rotational spectroscopy as shown in Figure 3.1 is a result of which molecular motion can be stimulated in a certain range of the electromagnetic spectrum. Full rotational spectroscopy is usually done in the microwave range, whereas infrared techniques are used in the detection of molecular vibrations. Vibrational spectroscopy is of interest in the gas analysis because the changes in potential energy between two states is much larger than that of rotational energy levels. Examples of instruments using vibrational spectroscopy are FTIR and NIR-LAS spectrometer.

Raman spectroscopy is another technique that detects molecular vibrations. A coherent light beam (laser) excites molecules to a virtual state which then drop back from the excited energy level to a different vibrational or rotational level. This slightly alters the wavelength of the photon released during the energy state change. This
3.2 Fundamentals of spectroscopy

Raman scattering is then dispersed and can be detected by a detector (CCD camera) to give a spectrum. As mentioned previously (section 2.5), Raman spectroscopy has been used in CVD analysis of CVD processes before (Beshkov et al. 2003; Davis and Pemble 1999; Boscher et al. 2008).

In CVD, the deposited films are routinely investigated with X-ray diffraction to determine the structure of the crystalline films. This technique however requires a sample to be processed off-line (Davis, Benito et al. 2004; H. Zhao, Q. Liu, Cai et al. 2008; Sheel, H. M. Yates et al. 2009).

3.2.2 Vibrational-rotational spectroscopy

Although drawn as straight lines in schematics and therefore implying a rigid connection between molecules, atoms in molecular systems can vibrate as depicted below for the example of CO$_2$ and HCl (Figure 3.2).

![Vibrational modes of CO$_2$ and HCl](Hollas 2002)

At atmospheric temperature most molecules are in their ground vibrational state $\psi = 0$. Because of the discretized nature of quantum states, molecules can jump to other vibrational states when they are excited by electromagnetic radiation (Hollas 2002).

It can be shown that the single vibration of a diatomic molecule such as HCl can be treated as a harmonic oscillator where the molecular bond is treated as a spring with a bond specific force constant. A more refined approximation shows that the bond vibration is more precisely described as an anharmonic oscillator (Banwell et al. 1994).
In absorption spectroscopy the transition from the vibrational ground state ($\psi = 0$) to the first excited state ($\psi = 1$) is the most prominent and can be observed in the (mid-)infrared with FTIR or grating spectrometers. The treatment as an anharmonic oscillator allows for the existence of other vibrational states besides $\psi = 1$ ($\psi = 2, \psi = 3$, etc.) which are known as overtone vibrations. Overtone vibrations are much weaker than the $\psi = 1$ vibration but can be observed in the near-infrared region of light with FTIR or laser absorption spectrometers.

It can also be seen that for a diatomic molecule, such as HCl, different rotational energy levels are populated (Boltzman distribution) in the ground and excited state (Figure 3.3). This leads to the formation of two branches in an infrared absorption spectrum, dependent on the change of angular momentum of the molecule ($\Delta j = \pm 1$). This results in a fine-structure in the spectrum, where sharp peaks in the spectrum are separated along the frequency axis by the change in angular momentum (Figure 3.4).

Per rotational level two peaks can be observed due to the fact that HCl presents two isotopes with slightly different masses and therewith a small variation in angular momentum. If the rotational quantum number $j$ is identical in the ground and excited state, a Q-branch can be observed. This is the case mostly in polyatomic molecules or diatomic molecules with electronic angular momentum in the ground state (e.g. NO) (Hollas 2002). For the HCl molecule the $j = 0$ transition from $\psi = 0 \rightarrow \psi = 1$ is forbidden and hence no Q-branch is observed.

Polyatomic molecules with N atoms present 3N degrees of freedom. The translation of all atoms together in three dimensional space as well as the molecular rotation in space does not alter the distance between atoms nor the angle. Therefore these six motions are deducted from the total number of degrees of freedom. This leaves 3N-6 vibrational degrees of freedom and if molecules are linear 3N-5 vibrations remain because there is no change in atom positions if the molecule rotates around its own axis (Hollas 2002).

To some extent the vibrations in polyatomic molecules can be treated as independent, leading to group vibrations. Similar molecules therefore present similar group vibrations because parts of the molecule are identical (e.g. C–H bonds). This can make it difficult to identify these molecules with infrared spectroscopy when present in a mixture because the spectral bands overlap. At wavenumbers below 1500 cm$^{-1}$, however, molecular vibrations are observed which incorporate multiple atoms in the molecule and therefore are less localized than specific group vibrations. For this
3.2 Fundamentals of spectroscopy

Figure 3.3: Excitation from the vibrational rotational ground state $\psi = 0$ to the first excitation state of the HCl molecule $\psi = 1$ with rotational states $j$ (redrawn from (Hollas 2002))

reason the spectral region of 1500 to 500 cm$^{-1}$ is called fingerprint region because vibrations in this spectral region tend to be characteristic for certain molecules (Smith 2011).

Also in larger polyatomic molecules the rotational energy levels are more complex compared to those of diatomic molecules such as HCl. The change in angular momentum is finite and no spectral fine structure can be resolved and only a broader envelope peak is observable. This is the case for many APCVD precursors for tin oxide deposition such as MBTC. The molecule presents no fine structure but an intense peak resulting from the C–H group vibrations and a fingerprint region in the lower wavenumber range from about 1500 to 500 cm$^{-1}$ (Figure 3.5) It can be seen that a molecule with a similar carbon chain as MBTC, Butane, presents similar vibrations around 2900 cm$^{-1}$ but a different fingerprint region.
3.2 Fundamentals of spectroscopy

**Figure 3.4:** Spectrum of hydrogen chloride in the mid-infrared region (simulated by spectralcalc (Spectralcalc))

**Figure 3.5:** FTIR spectrum of MBTC and Butane (data from (NIST Standard Reference Database 69 2009))

### 3.2.3 Beer-Lambert Law

Absorption spectroscopy is based on the Beer-Lambert law. It allows to measure the concentration of a liquid or gas sample by measuring the absorption of light by a specific molecule. An emitted photon with a certain energy level can be absorbed by a molecule. During this process the photon energy is transferred to the molecule,
promoting a change in the energy level of the molecule (Figure 3.6a). The Beer-Lambert law is a measure to calculate the concentration of a sample by observing the decay in light intensity through a sample of a given path length through absorption at a given wavelength (Figure 3.6b; Banwell et al. (1994)).

\[ E = h\omega = \frac{hc}{\lambda} \]

(a) Energy transfer through absorption

(b) Principle of the Beer-Lambert law. \( I \) is the light intensity, \( x \) a length and \( l \) the width of a gas sample

**Figure 3.6:** Photon energy transfer and principle of the Beer-Lambert law

Considering a sample of gas with a finite width \( \partial x \) and concentration \( c \) the incident light intensity \( I_0 \) decays through molecular absorption to the final intensity \( I_f \). The number of molecules \( N \) is proportional to the concentration in the volume of thickness \( \partial x \) (Banwell et al. 1994).

\[ N \propto c \cdot \partial x \quad (3.3) \]

The amount of intensity decay in the finite volume can then be expressed as

\[ \partial I = -\alpha \cdot c \cdot \partial x I \quad (3.4) \]

\[ \frac{\partial I}{I} = -\alpha(\lambda) \cdot c \cdot \partial x \quad (3.5) \]
where $\alpha(\lambda)$ is the absorption coefficient, a molecule specific and wavelength dependent value. To calculate the change in light intensity over the whole sample the following integral needs to be solved

$$\int_{I_0}^{I_f} \frac{\partial I}{I} = -\int_0^l -\alpha(\lambda) \cdot c \cdot \partial x$$

(3.6)

$I_0$ is the initial and $I_f$ the final light intensity, $l$ is the total sample thickness (path length).

$$\ln \frac{I_f}{I_0} = -\alpha(\lambda) \cdot c \cdot l$$

(3.7)

$$\frac{I_f}{I_0} = e^{-\alpha(\lambda) \cdot c \cdot l}$$

(3.8)

The final light intensity changes exponentially with the change of $c$ or $l$

$$I_f = I_0 \cdot e^{-\alpha(\lambda) \cdot c \cdot l}$$

(3.9)

Based on this, the absorption is calculated as

$$A = \ln \frac{I_0}{I_f} = \epsilon(\lambda) \cdot c \cdot l$$

(3.10)

with the molar extinction coefficient $\epsilon = \alpha \cdot \log(e)$. $\epsilon$ has units of $\text{L mol}^{-1} \text{cm}^{-1}$ and $c$ has the unit of $\text{mol L}^{-1}$.

Several formulations of the Beer-Lambert law exist whereas in infrared spectroscopy the absorption cross section $\sigma(\lambda)$ is often used. For this the absorption $A$ is expanded with the Avogadro constant $N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$ (Banwell et al. 1994).

$$A = \frac{\epsilon(\lambda)}{N_A} \cdot cN_A \cdot l$$

(3.11)

with

$$\sigma(\lambda) = \frac{\epsilon(\lambda)}{N_A} \text{ absorption cross section (cm}^2\text{)}$$

(3.12)

$$n = cN_A \text{ the absorber density (cm}^{-3}\text{)}$$

(3.13)
the absorption becomes

\[ A = \sigma(\lambda) \cdot n \cdot l \]  

(3.14)

In this form the absorption cross section contains all spectral dependencies. Considering the absorption cross section solely as a function of the wavenumber is only valid for constant temperature and pressure. To further separate these spectral influences the absorption cross section can be written as the product of a temperature dependent linestrength \( S(T) \) and a pressure dependent lineshape function \( g(\nu) \), where \( \nu \) is the wavenumber \( \nu = \frac{1}{\lambda} \).

\[ \sigma(\lambda) = S(T) \cdot g(\nu) \]  

(3.15)

At atmospheric pressure the lineshape function is the Lorentzian curve (see next section) and the linestrength can be calculated for many substances from tabulated values in the HITRAN database (Rothman et al. 2009). If a substance is not tabulated it is often practicable to measure the absorption cross section over the temperature range of interest to build up a database of absorption cross sections for a certain substance.

### 3.2.4 Broadening of spectral lines and lineshape functions

Although the absorption or emission of a species at a certain wavelength is referred to as spectral line, the lines are never fully monochromatic and a distribution around the central frequency can be observed even at high resolutions (Demtröder 2008). The function describing this distribution is the line function \( I(\nu) \) which is the result of a molecular energy transition whose energy difference \( \Delta E \) is defined as \( \Delta E = E_{\text{high}} - E_{\text{low}} \), the difference between high and a low energy levels. A significant variable derived from this distribution is the full width at half maximum (FWHM) which describes the peak width at half of the peak height (Figure 3.7).

The FWHM \( w_g \) and the centre wavelength \( \nu_c \) are used in various line shape functions in spectroscopy. Different line shape functions exist because of three phenomena. Due to Heisenberg’s uncertainty principle a natural width is inherent to every spectral line, but this effect is mostly negligible in industrial gas analysis as pressure and thermal broadening effects dominate. Thermal motion of molecules is dominant at low pressures where a Doppler velocity is imparted on each molecule, resulting in a Gaussian line shape function \( g_G(\nu) \) \( (P > 0.01 \text{ atm}) \).
3.2 Fundamentals of spectroscopy

With increasing pressure random molecule collisions perturb a molecule’s energy level resulting in a broadening effect due to pressure. At $P > 0.1\text{ atm}$ the pressure broadening effect dominates and the line shape follows the Lorentzian curve $g_L(\nu)$. This lineshape is common for infrared absorption spectroscopy at atmospheric pressure.

A third profile, the Voigt profile exists. It is a convolution of the gaussian and Lorentzian lineshape function $g_v = g_G \otimes g_L$ and can be used in the transition region between Doppler and pressure broadening. Towards higher pressures, when the Lorentzian FWHM is much larger than the Doppler FWHM $w_L >> w_D$, the Voigt profile reduces to the Lorentzian line shape and vice versa to the Gaussian line shape if $w_L << w_D$ (Banwell et al. 1994; Demtröder 2008). Data of spectral line positions and their changes with temperature and pressure are recorded in the HITRAN database. The HITRAN database allows to calculate spectra based on tabulated data (Rothman et al. 2009).

Table 3.1 summarizes the above mentioned lineshape functions and Figure 3.8 shows a plot of the Gaussian and Lorentzian functions for identical FWHM. It can be seen that height of the Lorentzian profile is much smaller compared to the Gaussian profile. Both peaks have an identical FWHM and area. The Lorentzian line kernel is narrower but the fall-off at the side of wings is slower, resulting in a larger contribution to area in the wing region of the line.
3.2 Fundamentals of spectroscopy

Table 3.1: Lineshape and FWHM functions for fitting to spectral data in Origin

<table>
<thead>
<tr>
<th>Profile</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaussian profile</td>
<td>$g_G(\nu) = B \cdot e^{-\frac{1}{2} \left( \frac{\nu - \nu_c}{w} \right)^2}$ $w_G = \sqrt{\ln(4)} \cdot 2w$</td>
</tr>
<tr>
<td>Lorentz profile</td>
<td>$g_L(\nu) = \frac{B}{\pi} \cdot \frac{1}{1 + \left( \frac{\nu - \nu_c}{w} \right)^2}$ $w_L = 2w$</td>
</tr>
<tr>
<td>Voigt profile</td>
<td>$g_V(\nu) = B \cdot \int_{-\infty}^{\infty} \frac{e^{-t^2}}{w_G^2 + \left( \frac{\nu - \nu_c}{\sqrt{2w_G}} - t \right)} dt \cdot \frac{1}{\int_{-\infty}^{\infty} \frac{e^{-t^2}}{2w_G^2} dt}$ $w_V = 0.5346 \cdot w_L + 0.2166 \cdot \frac{w_L^2 + w_G^2}{2 \ln 2}$</td>
</tr>
</tbody>
</table>

$(\text{Träger 2011; Banwell et al. 1994; OriginLab n.d.)}$

$B$ is the amplitude (the maximum of the measured spectra), $w$ is a width parameter which is initialized as $w = B/1.064$ for fitting to the Gaussian profile and $w = B/1.57$ for the Lorentzian profile, $\nu_c$ is the line centre (the corresponding value to $B$ on the frequency axis) and $\nu$ the control variable.

![Figure 3.8](image-url)  

**Figure 3.8:** Comparison of the Gaussian and Lorentzian lineshape function with identical FWHM (indicated by arrows)
3.2.5 Semiconductor detectors

In infrared absorption spectroscopy semiconductor detectors are placed at the end of the absorption path. The most simple devices consist of a thin single layer of semiconductor in between two electrodes. Initially the electrical resistance is high but is lowered if light shines onto the sensor. The reason is that incident light promotes electrons in the semiconductor to the conduction band. Single layer devices however are only used in simple applications due to their slow response time in the order of milliseconds and their non-linearity (Demtröder 2008, p. 200 ff.).

Much higher detectivity, linearity and much faster response time can be achieved through the usage of multi layer semiconductor materials that form a diode. Similarly to laser diodes, photodiodes form a p-n junction between semiconductor materials. Photoconductive and photovoltaic diodes exist. Photovoltaic diodes measure the change in voltage across the open circuit device, whereas in photoconductive diodes a current is induced by the incident light which is then converted into an analogue voltage signal through a precision load resistor. The response time of such detectors is in the pico-second range. Photoconductive diodes are available for wavelength ranging from the ultra violet to the infrared region of light.

For the detection of lasers operating in the near-infrared, indium-gallium-arsenide diode detectors provide a high detectivity from 800 to 1800 nm. These detectors operate at atmospheric temperature which make them a favourable choice for in-situ process monitoring compared to other material combinations requiring cooling through liquid nitrogen (Figure 3.9; Abramczyk (2005)). Cryogenic detectors, such as those based on mercury cadmium telluride, are often used in FTIR spectroscopy.
3.2 Fundamentals of spectroscopy

Figure 3.9: Detectivity over wavelength of popular infrared detectors. Popular room temperature detectors are marked red, cryogenic detectors are marked blue (W. Liu et al. 2007)

3.2.6 Optical fibres

Ultra-violet, visible and near-infrared light emitting from a light source can be coupled into fibre optic cables to transmit the light to the optical system. A fibre consists of three parts, a core, cladding and an outer coating. The outer coating is plastic material such as polyamide or silicone and protects the core and cladding mechanically. The cladding material is high purity quartz glass ($\text{SiO}_2$) and the core is also $\text{SiO}_2$ but doped with additives such as germanium dioxide ($\text{GeO}_2$) or phosphorus pentoxide ($\text{P}_2\text{O}_5$) which slightly raises the refractive index of the core compared to the cladding. The change of refractive index at the interface of core and cladding allows for total internal reflection to occur and light to propagate through the fibre with only small losses (Träger 2011, p. 1172).
Two types of optical fibre are distinguished, multi-mode and single mode fibres. The core of multi-mode fibres is thicker (50 to 1500 µm) compared to those of single mode fibres (3 to 9 µm). Multi-mode fibres allow the propagation of more than one wavelength, whereas single mode fibres constrain the propagation of light to a single optical mode. Single mode fibres are frequently used in the coupling of lasers where light of a single wavelength is transmitted.

Through recent advances in fibre manufacturing, multi-mode fibres for the mid-infrared region became available which makes them an interesting option for the use with FTIR spectrometers.

3.3 Fundamentals of diode laser absorption spectroscopy at atmospheric pressure

Lasers (light amplification by stimulated emission of radiation) are sources of coherent, directional and highly monochromatic light. They can be built from a wide range of materials and are used over a wide range of the light spectrum from the ultraviolet to the infrared. Applications range from cutting of metal and plastics to welding, medical use, communication, gas sensing and more (Träger 2011).

This work focusses on laser absorption spectroscopy in the near infrared for the detection of gaseous species and therefore the fundamental concepts covered in the following sections are limited to those relevant to the topic.

Tunable diode lasers (TDL) are coherent light sources whose wavelength can be tuned (within material limits). A range of different tunable laser types exists whereas
the semiconductor based lasers such as vertical cavity surface emission laser (VCSEL) are frequently used in gas sensing applications (Demtröder 2008). In semiconductor lasers the wavelength is tuned by controlling the temperature or pressure of the laser diode.

Semiconductor diodes are manufactured from various element combinations depending on the targeted wavelength range. Table 3.2 shows a summary of diode materials and their wavelength range.

**Table 3.2:** Summary of laser diode materials (Abramczyk 2005)

<table>
<thead>
<tr>
<th>Material combination</th>
<th>Wavelength range in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>350</td>
</tr>
<tr>
<td>ZnSe</td>
<td>525</td>
</tr>
<tr>
<td>AlGaInP</td>
<td>650–680</td>
</tr>
<tr>
<td>Ga0.5In0.5P</td>
<td>670</td>
</tr>
<tr>
<td>Ga1–xAlxAs</td>
<td>620–900</td>
</tr>
<tr>
<td>GaAs</td>
<td>900</td>
</tr>
<tr>
<td>In0.2Ga0.8As</td>
<td>980</td>
</tr>
<tr>
<td>In1–xGaxAsyP1–y</td>
<td>1100–1650</td>
</tr>
<tr>
<td>In0.73Ga0.27As0.58P0.42</td>
<td>1310</td>
</tr>
<tr>
<td>In0.58Ga0.42As0.9P0.1</td>
<td>1550</td>
</tr>
<tr>
<td>InGaAsSb</td>
<td>1700–4400</td>
</tr>
<tr>
<td>PbEuSeTe*</td>
<td>3300–5800</td>
</tr>
<tr>
<td>PbSSe*</td>
<td>4200–8000</td>
</tr>
<tr>
<td>PbSnTe</td>
<td>6300–29000</td>
</tr>
</tbody>
</table>

* Cryogenic temperature

Grey rows indicate the near-infrared region of light 800 to 2500 nm

The advantage of TDL is their high detection sensitivity down to the parts-per-billion volume (ppbv) range which allows the detection of trace amounts of gases in e.g. the earth atmosphere or in gaseous chemical reactions (Martin 2002).

Those lasers commonly operate at room temperature which makes them an interesting option for use in industrial applications. Further, through the advances in the communication industry, rugged solutions exist for the coupling of TDL light into optical fibres (see subsection 3.2.6).
3.3 Fundamentals of diode laser absorption spectroscopy at atmospheric pressure

Vertical cavity surface emitting lasers are TDLs based on semiconductor structures. In this layered structure, metal contacts on the top and bottom enclose the semiconductor, whereas one metal contact has a cylindrical hole as laser beam exit.

The laser light is emitted from a quantum well structure of only a few nanometre thickness in the core of the diode, commonly referred to as active region. With a current applied to the metal contacts the diode is forward biased and the electrons and holes are injected into the active layer where they recombine. For each electron-hole recombination a photon is released perpendicular to the layer (Figure 3.11). The semiconductor structure is enclosed by n- and p-type Bragg reflectors. These reflectors have a high total reflectivity (>99%) and are composed of multiple layers of alternating high and low refractive index materials such as aluminium arsenide and gallium arsenide.

The high mirror reflectivity is required to compensate for the thin active layer. Each reflector layer has a thickness of a quarter of the laser wavelength. This thickness is referred to as quarter wave optical thickness (QWOT). At each layer interface a part of the optical wave is reflected and the partial reflections constructively interfere, forming a resonator. The coherent laser light emits perpendicular to the semiconductor and through a cylindrical cutout of the otherwise opaque front metal contact (Träger 2011, p. 403).

![Diagram of Vertical Cavity Surface Emitting Laser diode and energy band structure](image)

**Figure 3.11:** Basic structure of a Vertical Cavity Surface Emitting Laser diode and detailed view of the energy band structure in the active region.
3.4 Fundamentals of FTIR spectroscopy

Molecules or molecule groups are infrared active if the molecule vibrations due to absorption of infrared radiation cause a shift in the dipole moment. These infrared active molecules absorb infrared light at different wavelength which makes infrared spectroscopy a valuable technique for the identification and quantification of molecular species. The most commonly used type of infrared spectroscopy is Fourier transform spectroscopy (Smith 2011). In a FTIR spectrometer the entire range of the mid-infrared spectrum is recorded during a scan whereas in conventional grating spectrometers only a narrow band of the infrared spectrum is recorded. Along with the fast acquisition of spectra and the broad wavelength range FTIR spectrometer are favourable for gas phase analysis and identification of gaseous species.

FTIR spectrometers are based on light interference created by an interferometer. The most commonly used interferometer is the Michelson type (Demtröder 2008).

3.4.1 Michelson interferometer

In a Michelson interferometer, infrared light is emitted by a radiation source which incidents on a beam splitter with ideally 50% transmittance and 50% reflectance. Half the light is transmitted onto a fixed mirror whilst the other beam is reflected onto a moving mirror. The two beams recombine at the beam splitter from where they are guided through a sample onto a detector (Figure 3.12; Smith (2011)).

Assuming for a moment that the FTIR light source is monochromatic and that the two mirrors are equidistant from the beamsplitter, the two light beams travel the same distance at the same speed. They are said to be in phase with each other at that point and will constructively interfere. This means that the amplitude of both signal will add to each other. If the mirror is displaced by one quarter of the incoming beam’s wavelength (\( \frac{1}{4}\lambda \)) the light incident on the moving mirror travels \( \frac{1}{2}\lambda \) further compared to the stationary mirror. This causes the two beams to be completely out of phase and they will destructively interfere to a zero amplitude. The optical path difference is commonly referred to as \( \delta \) where \( \Delta \) is the maximum mirror displacement (Hollas 2002).

The light source of a FTIR spectrometer is polychromatic but the principles of the interferometer are more easily understood considering a monochromatic lightsource.
at first. Further, it is assumed that an ideal beamsplitter exists. This would give the
irradiance at the interferometer the form (Bell 1972)

$$I'(\delta) = \frac{1}{2}I(\nu) + \frac{1}{2}I(\nu)\cos(2\pi\nu\delta) \quad (3.16)$$

$$= \frac{1}{2}I(\nu)(1 + \cos(2\pi\nu\delta))$$

The first part of the equation is constant and usually omitted. The part which
contains the modulated term is commonly named interferogram

$$I(\delta) = \frac{1}{2}I(\nu)\cos(2\pi\nu\delta) \quad (3.17)$$

Real beamsplitters will have a varying response over the total wavelength range
and also the detector has a wavelength dependent response function. The detector
signal amplifier contains certain filters to cut out undesired frequencies of light.
These instrument dependent factors are often summarized in a function $H(\nu)$. With
$B(\nu) = H(\nu)I(\nu)$ the above equation becomes

$$I(\delta) = B(\nu)\cos(2\pi\nu\delta) \quad (3.18)$$
3.4 Fundamentals of FTIR spectroscopy

\( B(\nu) \) is the instrument-function corrected irradiance of the source at wavenumber \( \nu \). In order to obtain the spectrum a Fourier transform of the interferogram \( I(\delta) \) is required (Griffiths et al. 2008).

For now the source was considered to be monochromatic whereas it is polychromatic in real FTIR spectrometers. The interferogram therefore becomes the integral over all wavenumbers

\[
I(\delta) = \int_{-\infty}^{+\infty} B(\nu) \cos(2\pi\nu\delta) \, d\nu
\]  

(3.19)

The spectrum \( B(\nu) \) is then obtained through the Fourier transform of \( I(\delta) \).

\[
B(\nu) = \int_{-\infty}^{+\infty} I(\delta) \cos(2\pi\nu\delta) \, d\delta
\]

(3.20)

Figure 3.13 shows a Fourier transform of a single cosine wave. The result is a plot with a single point which represents frequency of the input wave.

Up to now the equation considers the optical path inside of the spectrometer as an infinite distance. In reality, however, the mirror only moves a finite distance \( L \).

\[
B(\nu) = \int_{-L}^{+L} I(\delta) \cos 2\pi\nu\delta \, d\delta
\]

(3.21)
This truncation of the spectrum is mathematically identical to the multiplication of the interferogram with the boxcar function. The boxcar function has a 0 value except of an interval of length \( \Delta \) where it becomes 1.

\[
F(\delta) = \begin{cases} 
1 & \text{for } 0 \leq \delta \leq \Delta \\
0 & \text{for } \delta > \Delta
\end{cases}
\] (3.22)

### 3.4.2 Apodization

The Fourier transform of the boxcar function results in a sinc function. This sinc function introduces sine waves terms to the cosine waves which causes broadening of the lines (Figure 3.14; Mertz (1967)).

\[
\Gamma \{F(\delta)\} = \int_{-L}^{+L} I(\delta) \cos 2\pi \nu \delta \, d\delta
\]

\[
= \frac{2L \sin(2\pi \nu L)}{2\pi \nu L}
= 2L \text{sinc}(2\pi \nu L)
\] (3.23)

Several functions exist to suppress this effect. These functions are called apodization functions whereby the Norton-Beer set of apodization functions are the most popular (Norton et al. 1976; Naylor et al. 2007). The functions are defined in a way such that the sidelobes of the convoluted function become zero.

The original Norton-Beer function is given as

\[
f_{NB} \left( \frac{\delta}{L} \right) = \sum_{i=0}^{n} C_i \left[ 1 - \left( \frac{\delta}{L} \right)^2 \right]^i
\]

(3.24)

where \( \sum_{i=0}^{n} C_i = 1 \) with \( n = 0, 1, 2, \ldots, n \)

with the coefficients from Table 3.3. In this work the medium Norton-Beer function was used. The comparison of the sinc and the Norton-Beer function is depicted in Figure 3.15. The Norton-Beer function efficiently damps the ringing of the sinc function (Norton et al. 1976).
3.4 Fundamentals of FTIR spectroscopy

(a) Truncation of a wave due to the limited mirror path of the interferometer
(b) Broadened peak due to convolution with the sinc function

Figure 3.14: Truncation of the continuous wave function through the sinc function and the resulting Fourier transform with the broadened peak and superimposed sine-wave components

Figure 3.15: Comparison of the Norton-Beer apodization function to the sinc function
Table 3.3: Original Norton-Beer apodization function coefficients

<table>
<thead>
<tr>
<th>Apodization effect</th>
<th>$C_0$</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>weak</td>
<td>0.5480</td>
<td>-0.0833</td>
<td>0.5353</td>
<td>0</td>
</tr>
<tr>
<td>medium</td>
<td>0.26</td>
<td>-0.154838</td>
<td>0.894838</td>
<td>0</td>
</tr>
<tr>
<td>strong</td>
<td>0.09</td>
<td>0</td>
<td>0.5875</td>
<td>0.3225</td>
</tr>
</tbody>
</table>

Coefficient $C_3$ is 0 for all cases and was omitted.

3.4.3 Phase correction

The phase correction is the last step in the spectral processing from interferogram to a single line spectrum. Most commercial instruments have an in-built phase correction which constrains the user to a given method. The Mertz method is the most common phase correction in FTIR spectrometers (Mertz 1967).

Phase shifts in the spectrum mostly arise due to the following influences:

**Optical errors**: The path through the beamsplitter is slightly different for some wavelengths and therefore there exists no point where all wavelength completely constructively interfere. Misalignment of mirrors also contributes to a phase error.

**Sampling error**: The interferogram is evaluated at discrete points. The point of zero retardation (equal mirror distance) is unlikely to fall on a sampling point, causing a shift in the interferogram.

**Electronic errors**: Due to frequency filtering, signal amplification and non-linear detector performance.

The result is an added phase shift term to the to the spectrum. Equation 3.19 then becomes:

$$ I(\delta) = \int_{-\infty}^{+\infty} B(\nu) \cos(2\pi\nu\delta - \epsilon) \, d\nu $$

The effect of a shift in phase is the addition of sine terms to the interferogram because of $\cos(\alpha - \beta) = \cos\alpha \cdot \cos\beta + \sin\alpha \cdot \sin\beta$. This introduces imaginary parts.
In contrast to FTIR spectrometers, grating spectrometers do not operate with interference patterns of light but with diffraction of light by a prism or grating in order to disperse the light (James et al. 1969). The core of such a spectrometer is the monochromator, an arrangement of slits, mirrors and a light diffracting object (prism or grating). Light from a broad infrared light source is focused onto a narrow inlet to the Fourier transformation. With the use of Euler’s formula \( \cos \alpha - i \sin \alpha = e^{-i\alpha} \) Equation 3.25 can also be written as

\[
I(\delta) = \int_{-\infty}^{+\infty} B(\nu)e^{-2\pi i \nu \delta} d\delta
\]

which is a complex Fourier transform (Griffiths et al. 2008). The Fourier transform pair of Equation 3.26 is

\[
B(\nu) = \int_{-\infty}^{+\infty} I(\delta)e^{-2\pi i \nu \delta} d\delta
\]

For each measured spectrum \( I(\delta) \) the complex spectra \( B'(\nu) \) is obtained with its real and imaginary part

\[
B'(\nu) = Re(\nu) + i Im(\nu)
\]

By drawing this relationship in the complex plane and applying trigonometric theorems it is found that real and imaginary spectrum are related by the phase angle \( \epsilon \) (Griffiths et al. 2008).

\[
B'(\nu) = |B(\nu)| e^{i\epsilon}
\]

Based on Equation 3.29 \( B(\nu) \) can be written as

\[
B(\nu) = Re(\nu) \cos \epsilon + Im(\nu) \sin \epsilon
\]

By rearranging this equation and using trigonometric relationships it can be found that the phase angle is

\[
\epsilon = \arctan \frac{Im(\nu)}{Re(\nu)}
\]

which allows the phase correction of the measured intensity spectrum (Rahmelow et al. 1997; Griffiths et al. 2008).

### 3.5 Infrared diffraction grating spectrometry

In contrast to FTIR spectrometers, grating spectrometers do not operate with interference patterns of light but with diffraction of light by a prism or grating in order to disperse the light (James et al. 1969). The core of such a spectrometer is the monochromator, an arrangement of slits, mirrors and a light diffracting object (prism or grating). Light from a broad infrared light source is focused onto a narrow inlet.
3.5 Infrared diffraction grating spectrometry

slot from which the light travels onto a second mirror, which ideally is parabolic. This mirror then casts a parallel light beam onto the diffraction grating which separates the light into its wavelength. In the Littrow arrangement the diffracted light is reflected back onto the mirror towards a detector. In the Czerny-Turner arrangement a second mirror is used to reflect the light out of the monochromator. Other arrangements exist as well but the two mentioned are the most popular (James et al. 1969). Detector array spectrometers are common in the near-infrared, ultra-violet and visible region of light.

If a photodetector is used, the grating has to be rotated in order to focus light of different wavelength onto the single detector. Array detectors can also be used to detect a range of wavelength simultaneously without rotating the grating.

The instrument in this work uses the Littrow configuration with a spherical mirror. Compared to the ideally used parabolic mirror this introduces some aberration, but is also considerably lower cost. The detector is a pyro-electric array detector with 510 detector elements (Richardson et al. 1990; Ji et al. 2004).

![Diagram of Littrow monochromator with spherical mirror and array detector element](image)

Figure 3.16: Littrow monochromator with spherical mirror and array detector element

The spectral region observable is dependent on grating properties such as the blaze angle and the separation between grating lines. The blaze angle for the desired wavelength range can be calculated from

\[
\phi_G = \arcsin \left( \frac{\alpha \cdot \lambda}{2 \cdot s} \right)
\]

(3.32)
where $\phi$ is the angle of diffracted light from the grating normal, $o$ the refraction order, $s$ the separation of grating lines (here 100 lines/mm) and $\lambda$ the wavelength of interest (Palmer et al. 2005).

The intensity of light reflecting back from the grating surface $I$ can be calculated from

$$I = \frac{I_0}{S^2} \cdot \frac{\sin b}{b} \cdot \frac{\sin S_n \cdot a}{\sin a}$$  \hspace{1cm} (3.33)

with $I_0$ as the incident light intensity, $S_n$ the number of slits the light passes through after diffraction, $b = \pi \cdot \frac{s}{\lambda}$ where $s$ is the spacing of lines on the grating (in wavelength units) and $\lambda$ the wavelength. $a = \pi \cdot \frac{\sigma}{\lambda}$ where $\sigma$ is the spacing of the slits (James et al. 1969).

The resolution of a grating, $P_g$, can be calculated with

$$P_g = oN_g = \frac{\lambda}{\delta\lambda}$$  \hspace{1cm} (3.34)

where $N_g$ denotes the total line number on the grating and $\delta\lambda$ is the resolvable distance in wavelength between adjacent grating lines.

The resolution of the total instrument depends on numerous other factors such as mirror types used (spherical, parabolic), mirror efficiency and detector properties. Further, when using pyro-electric detector arrays, a chopper wheel is needed before the monochromator because the detector does only detect changes in light intensity. The frequency of the chopper wheel also has an effect on resolution with higher frequencies lowering the resolution because of the limited detector response time (Palmer et al. 2005).

### 3.6 Computational Fluid Dynamic simulations

Computational Fluid Dynamics (CFD) is the general term used to describe the solving of fluid flow problems with numerical methods. Simulations include the object’s geometry or a cross-section of it as well as a definition of all fluids present in the system and their interaction and effects on boundaries of the simulated object. Chemical reactions can be modelled through a chemical reaction mechanism which, in case of CVD, defines gas phase and surface reactions. The numerical solution accuracy depends largely on precise boundary conditions such as surface temperatures, flow
rates and material properties. The validation of numerical simulation results with experimental data is therefore important.

3.6.1 The Fluent CFD code

Fluent is a commercial software package developed and distributed by Ansys Inc. It is a multi purpose CFD software with the capability to model fluid flow and heat transfer in complex geometries and was used previously in the modelling of CVD processes (Chelimarios et al. 2012; M. Li et al. 2006; Tian et al. 2011; K. Kaneko et al. 2013; van Mol 2003). Although other CFD software packages exist which offer similar capabilities, Fluent remains a popular choice (Phoenics CFD; Kuijlaars et al. 1995; Wolf et al. 1999; Popovska et al. 1997; A. Li et al. 2008). The Fluent solver is able to process 2D and 3D models with axes symmetry, in steady-state or transient flows. Flows can be inviscid, laminar or turbulent and consist of one or multiple fluids. Particularly for CVD the ability to model flows including homogeneous and heterogeneous reactions and surface deposition is of interest (Fluent Inc. 2003).

To describe the transport of substances in a CVD reactor numerically, the equations for mass, momentum and heat transfer must be solved as well as a chemical species balance in cases where chemical reactions are modelled as well (Taylor et al. 1993; Fluent Inc. 2003).

**Mass balance**

$$\nabla \cdot (\rho \mathbf{u}) = 0$$

(3.35)

**Momentum balance**

$$\nabla \cdot (\rho \mathbf{u} \mathbf{u}) = -\nabla P + \rho g + \nabla \left[ \eta \left( \nabla \mathbf{u} + (\nabla \mathbf{u})^T \right) - \frac{2}{3} \eta \left( \nabla \cdot \mathbf{u} \right) I \right]$$

(3.36)

**Energy balance**

$$c_p \nabla \cdot (\rho u T) = \nabla \cdot (\lambda \nabla T) - \sum_{i=1}^{N} j_i \cdot \frac{\nabla H_i}{M_i} - \sum_{i=1}^{N} \sum_{k=1}^{K} H_i \gamma_{ik} R_k^q$$

(3.37)

**Chemical species balance** (Allendorf, Hitchman et al. 2000)

$$\nabla \cdot (\rho u Y_i) = -\nabla \cdot j_i + M_i \sum_{k=1}^{K} \gamma_{ik} R_k$$

(3.38)
3.6 Computational Fluid Dynamic simulations

\[ c_p \text{ Heat capacity} \quad g \text{ Gravitational acceleration} \quad H \text{ Molar enthalpy} \]
\[ I \text{ Unit tensor} \quad j \text{ Diffusive flux} \quad M \text{ Molecular weight} \]
\[ P \text{ Total pressure} \quad R_k \text{ Reaction rate} \quad T \text{ Temperature} \]
\[ u \text{ Velocity vector} \quad \gamma \text{ Activity of species} \quad \lambda \text{ Thermal conductivity} \]
\[ \eta \text{ Dynamic viscosity} \quad \rho \text{ Density} \quad Y_i \text{ Mass fraction of species } i \]

\textit{Subscripts}
\[ i \text{ w.r.t } i^{th} \text{ gas species} \quad k \text{ w.r.t } k^{th} \text{ gas phase reaction} \]

Certain boundary conditions for a CVD reactor such as the gas inlet temperature, inlet species concentrations, system pressure and deposition temperature are known. Other quantities, however, need to be calculated. Often, especially for the precursor chemicals, experimental values to compute the diffusive flux, thermal conductivity and viscosity are not known and need to be estimated. Additionally, if chemical reactions are involved, the rate constants are required as input parameters as well. A number of methods known as \textit{kinetic theory} exist to estimate certain material properties. At atmospheric pressure the gases involved in a CVD reaction can be described as incompressible ideal gases which allows the use of kinetic theory models (Poling et al. 2001).

\subsection*{3.6.2 Ideal gas diffusion}

All CVD processes involve the transport of gases to the reaction chamber and the transport of volatiles to and from a substrate surface. For the deposition of transparent conductive oxides CVD processes are mostly operated at atmospheric pressure and at high temperatures to achieve a fast thin film growth on the surface (A. M. B. v. Mol, Chae et al. 2006).

At this pressure and temperature the growth of the film is not limited by chemical reactions but rather by diffusion of gaseous species onto the surface (Allendorf, Houl et al. 2006).
3.6 Computational Fluid Dynamic simulations

To calculate the interaction between species in the gas mixture due to diffusion, the Maxwell-Stephan equation needs to be solved (Fluent Inc. 2003; Taylor et al. 1993).

\[
\sum_{(j \neq i)}^{N} \frac{X_i X_j}{D_{ij}} (\vec{V}_j - \vec{V}_i) = \vec{d}_i - \frac{\nabla T}{T} \sum_{(j \neq i)}^{N} \frac{X_i X_j}{D_{ij}} \left( \frac{D_{T,j}}{\rho_j} - \frac{D_{T,i}}{\rho_i} \right) \quad (3.39)
\]

\(X\) denotes the mole fraction, \(\vec{V}\) the diffusion velocity which can also be expressed in terms of the diffusive flux \(\vec{V} = \frac{J}{\rho}\), \(D_{ij}\) the binary mass diffusion coefficient and \(D_T\) the thermal diffusion coefficient.

The driving force for mass diffusion \(\vec{d}_i\) in the Maxwell-Stephan equation simplifies to \(\vec{d}_i = \nabla X_i\), a concentration gradient, if the assumptions holds that the external force on all species in the mixture is same and that diffusion due to pressure can be neglected (Taylor et al. 1993; Fluent Inc. 2003).

The diffusive flux of a species can then be expressed as (Fluent Inc. 2003).

\[
\vec{J}_i = -\sum_{j=1}^{N-1} \rho D_{ij} \nabla Y_j - D_{T,i} \frac{\nabla T}{T} \quad (3.40)
\]

where \(Y_j\) is the mass fraction of species \(j\).

The quantities of precursor chemicals compared to the inert transport gas is commonly low. This property is often used to simplify the computation by the usage of the dilute approximation which is equivalent to the Fickian diffusion for ideal gases (C. Kleijn 1991). In this approximation the Maxwell diffusion coefficient, \(D_{ij}\), is simplified to the binary diffusion coefficient. In a multicomponent system, the diffusive flux is computed for each species pair independent from other species. The diffusion coefficient for a species pair \(D_{ij}\) is then expressed by the Chapman-Enskog equation (Poling et al. 2001, p. 11.5)

\[
D_{ij} = \frac{3}{16} \cdot \frac{\sqrt{4 \pi kT}}{n \pi \sigma_{ij}^2 \Omega} \cdot f_D \quad (3.41)
\]

where \(k\) is the Boltzmann constant, \(n\) the number density of molecules, \(M_{ij} = 2 \left[ \frac{1}{M_i} + \frac{1}{M_j} \right]^{-1}\) and \(f_D\) a correction factor. Under the assumption of an ideal gas the number density \(n\) can be expressed with the ideal gas law and molecular masses in
3.6 Computational Fluid Dynamic simulations

the same order, the Chapman-Enskog equation further simplifies to the definition used by the CFD software Fluent (Poling et al. 2001, Section 11-3).

\[
D_{ij} = 1.883 \times 10^{-3} \sqrt{\frac{T^3 (M_i + M_j)}{M_i M_j P \sigma_{ij}^2 \Omega_D}} \tag{3.42}
\]

where \( D \) is the Fick diffusion coefficient for the species pair \( ij \), \( T \) is the absolute temperature, \( P \) the pressure, \( \sigma \) a characteristic length, \( M \) the molar mass and \( \Omega \) the diffusion collision integral.

The diffusion collision integral and the characteristic length depend on the intermolecular force law between colliding molecules (Poling et al. 2001). If molecules are treated as perfect spheres whose interaction depends on their molecular radius and distance from each other, the intermolecular energy relation of two molecules is expressed by the Lennard-Jones potential (Poling et al. 2001, p. 11.6)

\[
\phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \tag{3.43}
\]

with \( \epsilon \) the characteristic Lennard-Jones energy and \( \sigma \) the characteristic Lennard-Jones length.

The length (Å) and the energy divided by the Boltzmann constant (units of K) are input parameters in Fluent and require specification.

Both parameters can be calculated by the diffusion collision integral (see Figure 3.17). Equation 3.43 consist of an attraction and a repulsion term. When two particles are located far apart, the possibility of bonding is essentially zero and thus the potential bonding energy can be assumed to be zero. If the particles approach each other and then bond eventually the potential binding energy becomes largely negative to a point where the particles are so close that they reach an energy minimum (\( \epsilon \)). Now, if the particles are pushed closer together by an external force, the electrons in the particle orbitals start to interact which results in a repulsive force and a steeply increasing energy as the particles attempt to maintain their electron configuration. The point where the potential binding energy of the repulsion equals zero is the characteristic length \( \sigma \). The point at which the energy is minimal is the energy parameter \( \epsilon \).
3.6 Computational Fluid Dynamic simulations

Figure 3.17: Schematic plot of the Lennard-Jones potential energy $\phi(r)$. $\sigma$ is the characteristic length and $\epsilon$ the minimum energy parameter. $r$ is a radius of molecular length.

In this form the equation is called Lennard-Jones (12-6)-function. It is known that this function is from theory only valid for polar molecule pairs but in practise this potential equation is also used for non-polar pairs, although extensions such as the Stockmayer (12-6-3) potential exists which contains an additional term for non-polar pairs (Mourits et al. 1977). Fluent also used the Lennard-Jones potential in its basic form.

Values for the diffusion collision integral are tabulated but for computational simulations functions are preferred. The Fluent documentation does not state the function used in the code internally, but an equation such as the one published by Neufield et. al is likely (Poling et al. 2001). This function is based on the dimensionless temperature

$$T^* = \frac{kT}{\epsilon_{ij}}$$

where $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$ and eight constants are used.

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}$$

Together with an empirical thermal diffusion equation the diffusive flux can be fully calculated (Fluent Inc. 2003).
3.6 Computational Fluid Dynamic simulations

3.6.3 Viscosity

The fluid viscosity is estimated with kinetic theory by using the Lennard-Jones potential in the Chapman-Enskog equation for viscosity. For a pure and monatomic gas the equation is given as (Mills 1995)

\[ \eta = 2.67 \times 10^{-6} \sqrt{MT} \frac{1}{\Omega_\eta} \]  \hspace{1cm} (3.46)

Neufeld postulates an equation for the estimation of the collision integral based on a function which employs the dimensionless temperature \( T^* \) (see above) and constants (Neufeld 1972).

\[ \Omega_\eta = \left[A(T^*)^{-B}\right] + C [\exp(-DT^*)] + E [\exp(-FT^*)] \]  \hspace{1cm} (3.47)

Other methods to estimate viscosity at higher pressures and for dense gases are discussed elsewhere (Poling et al. 2001).

Wilke developed an equation to estimate the mixture viscosity based on viscosities of pure species. The solution is a simplification of the rigorous kinetic theory through the introduction of the rigid-sphere model (Wilke 1950). The simplified equation has been proven to be quite accurate. Another important aspect is that the weighting is done with mole fractions \( X \), as it is expected from simple kinetic theory (Mills 1995).

\[ \eta_{\text{mix}} = \frac{\sum_{i=1}^{n} X_i \eta_i}{\sum_{j=1}^{n} X_j \Phi_{ij}} \]  \hspace{1cm} (3.48)

where

\[ \Phi_{ij} = \frac{1 + \left(\frac{\eta_i}{\eta_j}\right)^{\frac{1}{2}} \left(\frac{M_i}{M_j}\right)^{\frac{1}{4}}}{\sqrt{8 \left[1 + \left(\frac{M_i}{M_j}\right)^{\frac{1}{4}}\right]^2}} \]  \hspace{1cm} (3.49)

3.6.4 Thermal conductivity

Thermal conductivity is difficult to measure and mostly unknown for many precursors used in CVD. Thermal conductivity can however be estimated using kinetic theory within an accuracy of about 5–7% for many species (Poling et al. 2001, section 9-3). Elementary kinetic theory formulations in a basic form are only valid for monatomic
species which are treated as rigid spheres moving randomly at a mean velocity. The molar density is $n$ molecules in a unit volume and the mass density is the mass in a unit volume. It can be shown that in this case the thermal conductivity is

$$\lambda = (\text{const}) \frac{T^{0.5}}{M^{0.5} \sigma}$$

(3.50)

This equation is known to be inaccurate if molecules store energy in other forms than translational (Poling et al. 2001, p 10.1). For monatomic gases with no rotational or vibrational degrees of freedom Equation 3.51 can be used to estimate thermal conductivity (Poling et al. 2001, p 10.2).

$$\lambda = 2.63 \cdot 10^{-23} \left(\frac{T}{M}\right)^{0.5} \frac{\sigma^{2} \Omega}{c_{p,i} M_{i}}$$

(3.51)

Precursors and reaction species in CVD are, however, often polyatomic and/or polar. To expand the capability of kinetic theory, modifications to the fundamental kinetic theory were suggested. These additions are commonly referred to as Eucken models (Mason et al. 1962; Tondon et al. 1968; Sandler 1968; Hirschfelder 1957).

Within Fluent the thermal conductivity is calculated with the following equation (Hanley et al. 1969; Sandler 1968).

$$\lambda_{i} = \frac{15}{4} \cdot \frac{R_{i}}{M_{i}} \eta_{i} \left[ \frac{4}{5} \cdot \frac{c_{p,i} M_{i}}{R} + \frac{1}{3} \right]$$

(3.52)

The viscosity was calculated in Equation 3.46 and the specific heat $c_{p}$ can be calculated with

$$c_{p,i} = \frac{1}{2} \cdot \frac{R}{M_{i}} (f_{i} + 2)$$

(3.53)

where $f$ is the degree of freedom of the fluid and can be set by the user (Fluent Inc. 2003).

The total thermal conductivity of the gas mixture is then calculated through known quantities:

$$\lambda = \sum_{i} \frac{X_{i} \lambda_{i}}{\sum_{j} X_{j} \phi_{ij}}$$

(3.54)
3.6 Computational Fluid Dynamic simulations

with

\[
\phi_{ij} = \frac{\left[1 + \left( \frac{\eta_i}{\eta_j} \right)^{1/2} \cdot \left( \frac{M_i}{M_j} \right)^{1/4} \right]^2}{\left[8 \cdot \left(1 + \frac{M_i}{M_j}\right)^{1/2}\right]^2}
\]  

(3.55)

3.6.5 Thermal diffusion

The thermal diffusion (also known as Soret diffusion) describes the transport of molecular species driven by a temperature gradient. Large and heavy molecules such as the MBTC precursor tend to accumulate in lower temperature regions of the reactor, whereas small and light molecules diffuse in direction of the heated substrate. Thermal diffusion effects are small if the temperature gradients are small and the molecular masses are similar. In a CVD reactor large temperature gradients are often present and also large differences in molecular mass. Therefore the Soret diffusion becomes significant (Kuo 1986).

Within Fluent the thermal diffusion coefficient \( D_{T,i} \) is computed from an empirical derived expression (Kuo 1986; Fluent Inc. 2003).

\[
D_{T,i} = -2.59 \cdot 10^{-7} \cdot T^{0.659} \left[ \frac{M_i^{0.511}X_i}{\sum_{i=1}^{n} M_i^{0.511} X_i} - Y_i \right] \cdot \left[ \frac{\sum_{i=1}^{n} M_i^{0.511} X_i}{\sum_{i=1}^{n} M_i^{0.489} X_i} \right]
\]  

(3.56)

3.6.6 Density

Under the assumption of an ideal gas, the fluid density is calculated from the ideal gas law

\[
\rho_i = \frac{P}{RT M_i}
\]  

(3.57)

and the mixture density is defined using the composition of the mixture

\[
\rho = \frac{P}{RT \sum_i \frac{X_i}{M_i}}
\]  

(3.58)

where \( Y_i \) is the component mass fraction.
3.6 Computational Fluid Dynamic simulations

3.6.7 Chemical reactions

The chemical reaction pathway of the deposition system has to be included in the CFD simulation to allow for the prediction of chemical species distributions and surface deposition rate. For this the parameters describing the reaction must be given to the simulation software by the user. As part of the chemical species balance, Fluent predicts the local species mass fractions by solving the conservation equation.

\[
\frac{\partial}{\partial t} (\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \vec{J}_i + R_i + S_i
\]  

(3.59)

with \( R_i \) as the net rate of production of species \( i \) and \( S_i \) the rate of addition of the species from other reactions or from other user defined sources.

A net \( R_i \) for all reactions a species participates can be computed

\[
R_i = M_{w,i} \sum_{r=1}^{N_R} \hat{R}_{i,r}
\]  

(3.60)

where \( \hat{R}_{i,r} \) is the Arrhenius rate considering the creation and destruction of species \( i \) in the reaction \( r \).

\[
\hat{R}_{i,r} = k_{f,r} \prod_{j=1}^{N_R} [C_{j,r}]^{\eta_{j,r}^f} - k_{b,r} \prod_{j=1}^{N_R} [C_{j,r}]^{\eta_{j,r}^b}
\]  

(3.61)

The forward respectively backward reaction rate constant \( k_{f/b,r} \) is computed by an Arrhenius expression, \( C_{j,r} \) is the reactant/product molar concentration of species \( j \) and \( \eta_{j,r}^f, \eta_{j,r}^b \) are the rate exponents for reactant and product of species \( j \) in the reaction \( r \).

To compute the rate constants user input is required for the Arrhenius expression

\[
k_{f,r} = A_r T^\beta e^{\frac{-E_r}{RT}}
\]  

(3.62)

User inputs to the software are then \( A_r \), the pre-exponential factor, \( \beta \) a temperature exponent and \( E_r \) the activation energy. The universal gas constant \( R \) is provided by Fluent and the temperature \( T \) is computed in the energy balance.

In modelling CVD reactions, backward reactions are usually omitted as the thermal driving force practically makes them very unlikely.
3.7 Summary

A multitude of spectroscopic methods exist across the electromagnetic spectrum. For the industrial gas analysis and in-situ monitoring in CVD reaction systems optical absorption spectroscopy in the infrared appears to be the most promising technique because it allows in-situ monitoring in the reactor gas phase. Spectrometers such as FTIR can record a broad spectrum in the mid-infrared region of light which is particularly interesting for the analysis of APCVD tin oxide precursors. Further grating spectrometers of the absorption type also have the ability to record spectra of selected features in the mid-infrared region.

Tunable diode lasers operate in the near-infrared region of light due to material properties of the diode material. In contrast to the broad spectrum light used in FTIR and grating spectrometers, lasers are coherent light sources with a narrow wavelength tuning region. Diode laser absorption spectroscopy has the ability to monitor selected peaks of overtone vibrations in the near-infrared. This however requires molecules to have a sufficiently strong first overtone vibration and a spectral fine structure so that the peak is situated in the laser tuning range. This is the case for small molecules such as HCl or CH₄. Because diode lasers are highly sensitive and also can be fibre coupled they are of great interest in gas analysis.

For the prediction of flow patterns and gaseous species distribution in CVD reactors computational fluid dynamic can be used. This numerical approach involves a series of semi-empirical and theoretical differential equations which are solved simultaneously based on defined boundary conditions.
4 Experimental equipment

4.1 Introduction

A range of equipment was used throughout this work for the monitoring on an APCVD reactor. To understand the challenges involved in such equipment development, the APCVD reactor system used is described in detail first.

Next, the individual optical instruments are described along with depictions of the installation of these instruments in the APCVD reactor and their mode of operation. Further a separate setup was built to investigate the decomposition mechanism of the MBTC precursor which is described as well.

4.2 APCVD reactor

The APCVD reactor is of the moving substrate type with a stationary coating head and translating substrate. The principal experimental setup is schematically depicted in Figure 4.1.

The precursor is supplied through a bubbler with nitrogen as carrier gas. Optionally the bubbler can be by-passed for purging (Bour et al. 2008). Oxygen and water are added after the bubbler. Water is supplied through a syringe pump and immediately evaporated on contact with the tape-heated pipes (130°C). To increase the overall gas volume, balance nitrogen is mixed with the reactants. All gas flows are controlled by flow tubes, manually set to the desired gas flow rate.

The flow of precursor, $F_{MBTC}$, follows Dalton’s law of partial pressure (Equation 4.1) (Bour et al. 2008). The partial pressure $P_i$ of MBTC is expressed by an Antoine equation derived by van Mol (van Mol 2003). The concentration could be varied by total pressure, temperature and flow through the bubbler. All experiments were performed at atmospheric pressure and at a set bubbler temperature.

As a result the flow rate of MBTC is a function of the bubbler nitrogen flow rate and the partial pressure of MBTC at the set temperature.
4.2 APCVD reactor

\[ F_{\text{MBTC}} = \frac{X}{1-X} F_{\text{N}_2}^{\text{Bubbler}} \]  \hspace{1cm} (4.1)

\[ X = \frac{P_i}{P_{\text{total}}} \]  \hspace{1cm} (4.2)

\[ P_i = A - 1000 \frac{B}{T_{\text{Bubbler}}} \text{ Torr} \]  \hspace{1cm} (4.3)

with \( A = 9.1 \), \( B = 3.07 \), \( P_{\text{total}} = 760 \text{ Torr} \) where \( X \) is the mole fraction of MBTC.

Water is injected through a syringe and on contact with the heated pipe walls evaporation occurs. The water vapour volume flow is calculated from the mass flow rate of water and the specific volume at the pipe temperature.

\[ F_{H_2O}^{(g)} = \dot{M}_{H_2O} \cdot \nu(T) \]
\[ = F_{H_2O}^{(l)} \cdot \rho_{H_2O} \cdot \xi(T) \]  \hspace{1cm} (4.4)

with \( \rho_{H_2O} \) as the liquid water density at room temperature and \( \xi(T) = 1.84 kg/m^3 \), the specific volume of water at the pipe temperature of 130°C (Keenan et al. 1955).

The mass balance for the reactor can then be stated as:

\[ F_{\text{total}} = F_{N_2}^{\text{Bubbler}} + F_{\text{MBTC}} + F_{H_2O}^{(g)} + F_{O_2} + F_{N_2}^{\text{Balance}} \]  \hspace{1cm} (4.5)

Before entering the coating head, the gas mixture goes through a laminarizer where the gas is also distributed across the width of the reactor head. The mixture then flows vertically down a narrow inlet slot, impinges on the hot substrate, followed by its reactions in the coating zone and extraction past the reaction zone. As a safety measure, the coating heads have two extraction ducts. Whilst the inner extraction duct close to the reaction zone mainly extracts the reaction gases, the outer extraction draws in air from the surrounding atmosphere in order to shield the environment from toxic reaction gases. The coating head design used is depicted in Figure 4.2.

Whilst production glass lines provide a continuous substrate feed, the laboratory reactors used processes rectangular substrate samples (100 mm x 100 mm). In order to coat these samples uniformly, the susceptor is mounted on a single axis linear
Figure 4.1: Schematic setup of the coating systems. Feed section consists of bubbler with MBTC on hotplate, nitrogen as carrier gas, oxygen and water as reactants. Water is injected by a syringe pump. Coating head has a laminarizer, an inlet slot and extraction ducts. The substrate sits on a translating heated susceptor block. Pipes past the flow meters are tape-heated to 130 °C translation stage. This allows the susceptor to travel from left to right in and out from under the coating head (see Figure 4.3). As a result the whole sample area has equal contact time with the reaction gases. The overall thickness of the film can be controlled by the number of passes of the sample under the coating head.

The pipe temperature is only sufficient to keep MBTC in vapour phase, but the heated susceptor (600 °C) provides the thermal energy to decompose the precursor which ultimately leads to the deposition of SnO₂ on the substrate surface.
4.2 APCVD reactor

Figure 4.2: Bottom and side view of the APCVD reactor head with expected gas flow patterns

Figure 4.3: Translational movement of the susceptor for one pass of the substrate under the coating head. Speed can be adjusted and is commonly set to 3mm/sec
4.3 Near infrared diode laser absorption system

The laser system used is based on a vertical cavity surface emitting laser diode (VCSEL) and diode detectors (Demtröder 2008). These type of lasers are frequently used for gas sensing applications in the near-infrared (Shemshad et al. 2012). In the near-infrared HCl has two overtone bands at 1.2 µm and 1.7 µm. The used VCSEL operates in the 1.7 µm band (Figure 4.4). There are two isotopes H\(^{35}\)Cl and H\(^{37}\)Cl present whereas H\(^{35}\)Cl has an atmospheric abundance of 75.76% and H\(^{37}\)Cl 24.23% respectively. The scanned spectral feature in this work is the R(3) vibration-rotation transition of H\(^{35}\)Cl (Corsi et al. 1999; Martin et al. 2007).

**Figure 4.4:** Simulated transmittance spectrum of the first overtone of hydrogen chloride (1.7 µm) in the near-infrared. Simulation parameters: Path length: 10 cm; temperature: 633 K; volume mixing ratio: 0.1. Simulated by (Spectralcalc)
The laser is controlled by temperature and current through the diode. A thermoelectric cooling element ensures operation at the selected feature wavelength and wavelength tuning across the feature is achieved by ramping the current (B. Zhao 1999). The current is supplied by a National Instruments data acquisition board.

The laser light is coupled into a single mode fibre optical cable leading to an adjustable collimating lens which allows the collimation of the beam to under 1 mm in diameter (Träger 2011; Demtröder 2008). The focal point of the laser beam was set to the centre of the coating head. This is required for the beam to pass freely through the narrow reaction zone under the coating head (see subsection 4.3.2).

The laser signal is detected with one or two indium-gallium-arsenide diode(s) which convert the laser light into a voltage signal (Abramczyk 2005). This data is send to the data acquisition card mentioned above. A Labview software then displays and records the detector signal (developed by TDL sensors Ltd.).

For some experiments a beam splitter was used. This allowed monitoring with two beams simultaneously at different positions in the coating zone.

The laser launch and the photodiode detector are mounted on optical posts with identically constructed, multi axes adjustment (translation, rotation) brackets (Figure 4.5).

**Figure 4.5:** Setup of the laser monitoring system. Laser is controlled by a data acquisition board connected to a control PC. Laser launch and detector have full five axes adjustability. Rotation around x-, y- and z-axis and translation in z- and y-direction.
4.3 Near infrared diode laser absorption system

4.3.1 Signal processing

The photodiode detector is connected to a data acquisition card (National Instruments) which is connected to a PC via USB. A Labview program is used for data recording and control of the laser system. Data is recorded at a rate of 10 Hz.

The data acquisition card records spectra as a function of the current tuning range sampled with a 16 bit resolution. A typical recorded spectra can be seen in Figure 4.6. The aim of the monitoring process is the determination of a HCl concentration which is determined from absorption spectra (see subsection 3.2.3). This however requires the tuning range of the laser to be expressed in terms of wavenumbers (cm\(^{-1}\)) instead of sampling points. To find the conversion function from points to wavenumbers an etalon measurement is required. A Fabry-Perot etalon defines the separation of two transmission peaks as free spectral range (FSR; Demtröder (2008)). By knowing dimensions, material properties of the etalon as well as the temperature (affects the refractive index \(n_{\text{ref}}\)), the FSR can be calculated as

\[
\text{FSR} = \frac{1}{2 \cdot n_{\text{ref}} \cdot L_e} \text{cm}^{-1}
\]

Figure 4.6: Signal recorded by the photo detector
with \( n_{\text{ref}} \) being the refractive index of the etalon material and \( L_e \) the etalon length. For the etalon used the FSR was calculated to

\[
\text{FSR} = \frac{1}{2 \cdot 1.501 \cdot 3.79} = 0.088 \text{ cm}^{-1}
\]  

(4.7)

Placed into the laser beam, the etalon generates peaks separated by the FSR. Each peak in the tuning range can then be identified (e.g. with OriginLab (n.d.)).

Figure 4.7 shows a plot of the photo detector signal over the point range with marked peaks and wavenumber converted secondary x-axis. It can be seen that the separation between the peaks is evenly spaced by 30 points. Therefore \( 30 \text{ points} = \text{FSR of } 0.088 \text{ cm}^{-1} \). The relation between points and FSR is not necessarily linear and fitting of a polynomial conversion curve between points and FSR may be required in other cases. For the system used here, the laser tunes over a total of 0.5 cm\(^{-1} \) wavenumbers.

\[\text{Points in scan}\]

\[\text{Relative wavenumber cm}^{-1}\]

\[\text{Photo detector output}\]

\[0 \quad 0.05 \quad 0.1 \quad 0.15 \quad 0.2 \quad 0.25 \quad 0.3 \quad 0.35 \quad 0.4 \quad 0.45 \quad 0.5 \quad 0.55\]

\[0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1 \quad 1.2 \quad 1.4 \quad 1.6 \quad 1.8 \quad 2 \quad 2.2 \quad 2.4\]

\[0 \quad 20 \quad 40 \quad 60 \quad 80 \quad 100 \quad 120 \quad 140 \quad 160 \quad 180 \quad 200\]

\[\text{Scan start}\]

\[\text{Scan stop}\]

\[82 \quad 112 \quad 142 \quad 172\]

\[\text{Figure 4.7: Signal generated by the etalon over scan points and wavenumber and highlighted positive peak positions}\]
4.3 Near infrared diode laser absorption system

If the laser passes through a HCl containing volume, laser light is absorbed by the HCl molecules in the beam path at specific wavelength within the tuning range. As a result, the photo detector output is decreased at those wavelength as less light reaches the detector. In consequence, a peak can be observed in the photo detector output. The laser wavelength was controlled (by adjusting the laser diode temperature) in such a way that the peak centre was observed approximately at the midpoint of the linear current ramp (see Figure 4.6). The first 25 points of the recording can be omitted as those contain the steep falling edge from the previous ramp and a period of zero amplitude.

The remaining points represent the measured signal $I$. The absorbance is then calculated with Beer-Lambert’s law for gases (Banwell et al. 1994).

$$A = - \ln \left( \frac{I}{I_0} \right)$$  \hspace{1cm} (4.8)

where $I_0$ is the background signal. It is obtained by fitting a third order polynomial (see Equation 4.9) to the points of $I$ which are located outside of the peak. Fitting is performed with a least-square Levenberg-Marquart algorithm (Budil et al. 1996; Nash 1979).

$$f(x) = a + b \cdot x + c \cdot x^2 + d \cdot x^3$$  \hspace{1cm} (4.9)

Figure 4.8 shows the signal $I$, the calculated background $I_0$ and the points used in the least-square fitting of the background. The magnified region of the plot highlights the importance of carefully choosing the point range for calculating $I_0$. Choosing points too close to the peak signal would lead to an inaccurate extraction of the absorbance peak because the peak area would be truncated. The absorbance is then calculated with Equation 4.8 (see Figure 4.9).

At atmospheric pressure the peak shape is Lorentzian (Demtröder 2008) and follows the equation

$$g_L(\nu) = g_L(0) \frac{B}{\pi} \cdot \frac{1}{1 + \left( \frac{\nu - \nu_c}{w} \right)^2}$$  \hspace{1cm} (4.10)

with $g_L(0)$ is a baseline offset, $B$ being the peak amplitude, $w$ the width at half peak height (full width half maximum, FWHM) and $x_c$ the x-coordinate of the peak centre. By fitting this function to the experimental values, the peak area can be determined (see Figure 4.9).
4.3 Near infrared diode laser absorption system

**Figure 4.8:** Raw scan signal $I$ with fitted third order polynomial background $I_0$ and wavenumber range used for fitting

**Figure 4.9:** Extracted absorption peak of HCl and fit of a Lorentzian function

As mentioned above, this procedure is built into the Labview software but also all raw scans are saved. This allows for post-processing and the adjustment of fitting variables for each recorded spectra-series. Fitting is done with a non-linear least-squares Levenberg-Marquart algorithm within Labview. Outside of Labview a R-program (see below) allows post-processing of raw data with a modified Levenberg-Marquart algorithm (Nash 1979, Algorithm 23). The modified algorithm was chosen
because it proved to be more robust in fitting to the measurement noise floor because it provides enhanced support for bounds constraints (Nash 2013). At times when the substrate leaves the coating zone the HCl concentration becomes zero, leaving only a noise floor to which the algorithm attempts to fit a Lorentzian lineshape. In this situation, the standard implementation of the Levenberg-Marquart algorithm often failed because the initial guess provided was too far off. The R code can be found in section C.1 and Figure 4.10 shows a screenshot of the programming environment R-studio running this code. The R-project programme is a suite of software offering data manipulation, calculation and graphical display and in particular the handling of large data structures (RStudio; R Development Core Team 2013).

![Figure 4.10: Screenshot of the R-code processing recorded HCl spectra within the R-studio programming environment](image)

### 4.3.2 Laser beam collimation

It was found that a collimating lens is required on the launch side to collimate the beam to a diameter of \( \approx 1 \text{ mm} \) in order to let the beam pass freely through the reaction zone.

To ensure that the beam diameter is in the required diameter range over the whole path length, a beam profiler (Thorlabs, BP109-IR2) measured the beam diameter...
4.3 Near infrared diode laser absorption system

Figure 4.11: Comparison of 13.5\% beam diameters recorded with a Thorlabs BP109-IR2 in increasing distance from the lens. Red lines indicate the position of the lens and the coating head in the actual arrangement.

over the path length prior of installing the equipment in the reactor. A GRIN (gradient-index) lens (Thorlabs, 50-1550-APC) and an adjustable collimating lens (Thorlabs, CFC-2X-C) were tested (Demtröder 2008). Figure 4.11 compares the laser beam diameters of the two lens types. It shows that the beam is small enough in the region where it passes the coating head if the collimating lens is used. The grin lens beam diameter is comparatively larger and clipping of the beam on the coating head or the substrate could occur. Beam jittering, due to rapidly changing heat profiles in the reaction zone and therewith varying indices of refraction, is also observed during the actual monitoring process. While the photodiode detector element is large enough to compensate for the jitter, beam clipping can occur in the reaction zone if the beam is obstructed by the coating head or the glass substrate. For this reason it was found that the gap between coating head and substrate should not be smaller than \(\approx 2\text{ mm}\).
A setup was built which allows the decomposition of the MBTC precursor under various conditions (Figure 4.12). The design of the feed section follows the design of the APCVD reactor (section 4.2).

The MBTC precursor (Fisher Scientific, 97%) is in a bubbler vessel (built in-house) whose temperature is controlled by a hot plate (IKA C-MAG HS 4). Nitrogen (BOC, oxygen free) is supplied through a flow meter, flows through the bubbler and transports a MBTC-nitrogen mixture into the heated piping system (Swagelok 1/4 in pipes, heating tape from Electrothermal HT95506, temperature controller Barnstead Electrothermal MC 810). Optionally the bubbler can be bypassed by manually switching three valves. This was commonly used to purge the system between
measurements with the FTIR spectrometer. Heating of the pipe system (130°C) is necessary to avoid condensation of MBTC (Sheel and Gaskell 2011).

After the bubbler, the mixture enters an oven with a wide temperature range of 200 to 1000°C. The oven (Carbolite HST 12/200) is of the tubular type with a tube diameter of 60mm and a tube length of 480mm. A loop of pipe goes through the oven and then enters a second heated section of piping which flows the gas mixture into a heated optical cell (built in-house). Both ends of the cell are capped off with potassium bromide windows (Crystran, KBr 25 mm x 3 mm).

Past the cell, the gas mixture is condensed and gaseous components are vented through an exhaust pipe.

Further, oxygen (BOC, nitrogen free) or additional nitrogen can be added to the gas stream prior to the oven through a three-way-valve (Swagelok) and injection of liquid water is possible through a syringe pump (B. Braun Melsungen AG, 871104). The low liquid water stream of 0.16 to 0.81 mL h⁻¹ is assumed to fully evaporate at the pipe temperature of 130°C.

Monitoring is performed by a FTIR spectrometer (Bruker Equinox 55). A periscope, consisting of two 50 mm diameter planar gold mirrors (Thorlabs), redirects the infrared beam from the instrument through the optical cell. The periscope is required due to a difference in height between the instrument and the optical cell. Past the cell, the light is collected and collimated onto a mercury cadmium telluride (MCT) detector element (Infrared Associates, D315/6) by an off axis parabolic mirror. The detector operates at cryogenic temperatures and is cooled by liquid nitrogen (Smith 2011).

The spectrometer is controlled by a PC and temperature data from all measurement points is recorded continuously (PICO Tech. Ltd., TC-08) by the PC as well. All thermocouples used for temperature monitoring are of the K-type.

4.5 Grating spectrometer for measuring the MBTC concentration at the reactor inlet

In many CVD applications the precursor is delivered through a bubbler containing a liquid precursor, temperature controlled to a certain vapour pressure. A gas then
4.5 Grating spectrometer for measuring the MBTC concentration

Flows through the bubbler which transports the precursor into the gas stream. Such a bubbler system is also used in the APCVD of tin oxide from MBTC. The transport gas is nitrogen and the flow through the bubbler is controlled by a flow tube. By assuming a saturated vapour phase the flow of MBTC can be calculated by employing Dalton’s law of partial pressures (Bour et al. 2008).

\[
F_{\text{MBTC}} = F_{\text{N}_2} \frac{P_{i,\text{MBTC}}(T)}{P_{\text{total}} - P_{i,\text{MBTC}}(T)}
\]  

(4.11)

The temperature dependent partial pressure \(P_{i,\text{MBTC}}(T)\) can be calculated with Antoine’s equation. The equation is derived from the Clausius-Clapeyron equation and relates temperature and saturation vapour pressure in pure substances:

\[
\log g = A - \frac{B}{T}
\]  

(4.12)

whereas values for the constants \(A\) and \(B\) can be found in literature. For MBTC coefficients have been determined by A. M. B. v. Mol for the temperature range 70 to 140 °C (van Mol 2003, p. 91). This method has been used previously to determine bubbler fill levels (Bour et al. 2008). It is known, however, that the bubbler fill level has an influence on the precursor concentration leaving the bubbler (William J. Curran 2006). It is therefore desirable to monitor the gas flow out of the bubbler to ensure a constant precursor concentration in the reactor feed. A commercial system exists which is able to monitor precursor concentration in binary mixtures with an acoustic sensor (Composer ( Elite), Inficon Ltd.).

The instrument used here is a recently developed infrared grating spectrometer with the ability to monitor the precursor concentration in higher order mixtures and at a lower price compared to the commercial system (James et al. 1969; Palmer et al. 2005). The instrument can be connected to the existing pipework on a CVD reactor. The advantage of this system over an FTIR is its detector operation at atmospheric temperature, the absence of moving optical parts, small footprint and low price.

4.5.1 Instrument design

The instrument uses a 240 W tungsten halide lamp as an infrared light source. The infrared light beam is guided through a heatable sample cell (50 mm path length, KBr windows) by a combination of mirrors and lenses. Past the sample cell the light
4.5 Grating spectrometer for measuring the MBTC concentration

beam is focused onto the entrance slit of the monochromator. The monochromator uses the Littrow arrangement, consisting of a spherical mirror \( f = 100 \text{ mm} \) and a diffraction grating. The grating (300 lines per mm) is blazed for the spectral region of MBTC at around 2900 cm\(^{-1}\) (see Figure 4.14). The mirror guides the parallel light to the grating where it is separated into its wavelength and reflected back to the mirror at a slightly altered angle. Another mirror then guides the diffracted light onto a pyro-electric array detector (510 detector elements). Because the pyro-electric sensor detects changes in infrared intensity, a chopper wheel is in the beam path in front of the sample cell (Figure 4.13).

The narrower the inlet slot to the monochromator is, the better the resolution of the instrument but also less light enter the monochromator and there is a trade off between resolution (the ability to resolve nearby wavelength) and optical power through the system (James et al. 1969; Palmer et al. 2005). The detectivity and spectral resolution of the pyro-electric array detector is influenced by the IR radiation modulation frequency. Good quality measurement signals can be recorded for frequencies of up to 40 Hz. The detector is connected via USB to a laptop computer running a standalone data acquisition program written in Matlab.

The spectral region at 2900 cm\(^{-1}\) was chosen because of the broad and strong infrared absorption of the MBTC precursor in that region (see Figure 4.14).

![Figure 4.13: Setup and schematic of the infrared grating spectrometer](image-url)
4.5 Grating spectrometer for measuring the MBTC concentration

Figure 4.14: Infrared transmission spectrum of MBTC (FTIR, 1 cm\(^{-1}\) resolution). Marked peak (red) was selected for monitoring with the grating spectrometer

4.5.2 Calibration

Calibrating the spectrometer is necessary for quantitative measurements of the reactor inlet concentration. The spectrum of MBTC recorded with the grating spectrometer is compared to spectra recorded with the FTIR spectrometer (Figure 4.15a). It can be seen that the resolution of the grating spectrometer is lower in comparison and that less significant features can be resolved. Using Beer-Lambert’s law the absorption can be calculated from the recorded transmission spectra. Plotted over a range of known absorber concentrations it was found that a linear relationship exists between the integrated absorbance and the molar concentration of MBTC. This is an ideal precondition for quantitative measurements as the recording of a few spectra with known concentrations is sufficient to calculate the concentration of MBTC in the mixture over a wide range (Figure 4.15b).
4.5 Grating spectrometer for measuring the MBTC concentration

(a) Resolution adjusted FTIR spectrum of MBTC compared to grating spectrometer FTIR spectrum

(b) Integrated absorbance (blue) and single line absorption (red) of MBTC with fitted linear regression lines (green)

Figure 4.15: Grating spectrometer calibration data
5 Monitoring of APCVD process stability through *in-situ* and *in-line* spectroscopy

5.1 Introduction

TCOs are deposited on-line on floating class lines in APCVD reactors at high speed and temperatures. Monitoring the stability of the process and an early fault detection are desirable in an production environment for quality control and reduction of defective product output (Peng et al. 2008; Herman 1996). Detecting faults that lead to the deposition of films with undesired properties or structure at an early stage in the process is important with respect to potential material savings (see below, section 5.2). At process start-up monitoring can also aid in adjusting process parameters (precursor flow rates, temperatures) such that conditions which are known to yield films of desired properties are obtained. Spectroscopy techniques by themselves are probably unable to provide the ability for directly controlling the process through closed loop feedback (Allendorf, Bernard et al. 1997, p. 619), but they can be important in providing data for the modelling of the manufacturing process (Mönch et al. 2013).

The precursor is delivered through an evaporator or bubbler system, commonly with no other control besides temperature and pressure of the system. An *in-line* optical monitoring system can enhance the control of feed quantities to the coating system. Other flow rates to the reactor as well as temperatures of parts in the reactor are monitored rigorously but commonly no monitoring is done in the coating zone right under the coating head. Blockages in the feed pipes or partial blockages of the coating head can therefore be undetected. An *in-situ* monitoring system can provide valuable information about process stability and progress.

The installation of *in-situ* monitoring equipment is often difficult due to the high process temperature (873 K) and limited access to the reactor coating head.

A common fault in production is the (partial) blockage of pipes feeding the reactor. The pipes contain the precursor along with other reaction gases at a temperature below decomposition. Local hot- / cold-spots due to insufficient heating can cause the partial decomposition or condensation of reactants, contaminating the pipes and adding an uncertainty in regard to the amount of precursor actually fed to the system.
5.2 Potential material savings through in-line and in-situ process monitoring

Such blockages in the reactor coating head can also lead to undesired non-uniform film thickness.

This gives rise to the need for a monitoring system with the capability of measuring both, the precursor concentration entering the coating system and the process stability during the deposition in the APCVD reactor.

5.2 Potential material savings through in-line and in-situ process monitoring

Several optical techniques for product quality control exist, but usually those instruments are found at the cold end of the process (see section 2.5). Therefore a delay exists between the actual TCO deposition and subsequent quality control. Depending on the production line, this delay can be 20 to 30 min.

At line speeds of 500 to 900 m h\(^{-1}\) and a substrate width of 3 m, at least 500 m\(^2\) of defective product are produced before faults occurring in the APCVD process are detected (based on a monitoring point 20 min after deposition).

Enhanced reactor control is therefore an interesting technology for glass manufacturers as an instantaneous feedback of the deposition process can reduce the output of defective product and consequently cost.

5.3 Monitoring of process stability through in-situ near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

As gas flows in the reactor cannot be disturbed by physical objects because of the required film uniformity, a non-invasive technique is required. In-situ laser absorption monitoring is a well established technique to measure chemical species non-invasively in gas phase with high sensitivity. Optical access for laser absorption monitoring of gas phase concentrations of reaction molecules is possible through the small gap between the reactor coating head and the substrate, which allows one or more laser beams to pass through to a detectors on the opposed side of the coating head (see Figure 5.1 and Figure 5.2 in subsection 5.3.1).
5.3 Monitoring of process stability through in-situ near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

As explained previously, laser absorption monitoring in the near infrared is capable of detecting the overtone vibrations of molecules with fundamental vibrations in the mid-infrared (see section 4.3). The tin containing intermediate that initiates the growth on the surface is yet unknown and hence only reaction molecules with overtone vibrations are suitable for monitoring with near infrared diode laser absorption spectroscopy (NIR-LAS). This is in so far problematic as a direct relation between an observable molecule and film growth may not be given, e.g. if a chemical is produced in gas phase and on the surface simultaneously. Nevertheless, the robustness and sensitivity of near infrared systems along with their availability on the market make them a feasible choice for monitoring in-situ (Herman 1996).

Hydrogen chloride monitoring was identified as a versatile technique suitable for on-line monitoring of many tin oxide depositing CVD processes. The precursor molecules of common TCO precursors such as Tin-tetrachloride (TTC), Di-methyl-tin-trichloride (DMTC) or Monobutyl-tin-trichloride (MBTC) are chlorine based and hence hydrogen chloride can be observed during deposition from these precursors (Goshtagore 1978; Giunta et al. 1993; Allendorf, Houl et al. 2006).

As mentioned above, a distinct difference is, however, whether HCl is created during precursor decomposition in the reactor gas phase, in a surface reaction or in both due to secondary reactions. Monitoring the concentration of a reaction creating HCl in gas phase as the only chlorine containing species gives a direct relation to the precursor entering the reactor. This is not necessarily the case for surface created HCl because the formulation of the (chlorine containing) growth initiating intermediate molecule is often not known and neither is the possible formation of other chlorine containing intermediates which absorb light outside of the laser wavelength range.

Laser absorption monitoring of hydrogen chloride at multiple points on an APCVD reactor with MBTC chemistry for tin oxide deposition was carried out with the aims of

1. identifying the ideal monitoring positions in the reaction area
2. minimizing the number of laser beams required
3. monitoring the change of HCl concentrations during various process conditions
4. gaining the ability to estimate film quality based on the monitoring results.
5.3 Monitoring of process stability through in-situ near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

5.3.1 In-situ laser absorption monitoring measuring arrangement

The reactor used is a thermal APCVD reactor for the deposition of tin oxide from MBTC (see section 4.2). In this APCVD reactor a pre-heated gas mixture flow down a narrow inlet slot and impinges onto a hot glass substrate (commonly 873 K). Usually the film growth rate is highest where the gas stream impinges first on the substrate and the precursor concentration is the highest.

With increasing distance from this inlet gas stream the precursor is consumed in the reaction and precursor concentration and film growth rate decrease. The reactor used is of the dual flow type.

A stationary substrate would ultimately lead to deposited films of non-uniform thickness. To overcome this problem, the reactor operates with a stationary coating head and translating substrate. This technique allows for equal contact time of the gas stream with all areas of the glass substrate.

Figure 5.1 shows the cross section of the reactor with the expected flow patterns and the laser beam positions used throughout this work.

![Figure 5.1](image)

**Figure 5.1:** Cross section of the lab scale reactor with arrows illustrating the reactive gas mixture, the assumed air flow pattern and beam positions 1–11

As the gas mix enters the reaction zone, precursor decomposition occurs close to the surface due to the heat radiating from the substrate. The created tin intermediates
then form solid tin oxide on the substrate surface. Gaseous by-products created in this process desorb from the surface and diffuse back into the bulk gas stream.

Unreacted gas mix and gaseous reaction by-products are actively extracted by a two-stage extraction around the reaction zone. The negative pressure is created by fans operating at 20 Pa below atmospheric pressure. The outer extraction’s main purpose is to draw in air from the surrounding atmosphere to form an air curtain shielding the area outside of the reaction zone from toxic reaction gases. The bulk of the reactor gases are extracted in the inner extraction.

While the coating head is stationary and gas flows constantly down the inlet slot, the susceptor is mounted on a translation stage. The translational movement back and forth under the coating head ensures that the substrate is coated uniformly over its full length (see Figure 4.3).

The susceptor provides the heat needed for the reaction to occur. The temperature is variable but was set to 873.15 K for most experiments to ensure operation at the mass transfer limit. The temperature distribution is however not fully homogeneous as thermocouple measurements on the surface showed.

The moving susceptor, the small gap (1 to 2 mm) between coating head and substrate are and the overall width of the coating head are the limiting factors for optical access to the reactor. Furthermore, due to the requirement of spatial measurements in the reaction zone, the optical equipment requires a free translational path perpendicular to the gas inlet slot.

The optical set-up installed for this purpose is shown in Figure 5.2. It consists of a laser launch side and a detector side. The collimating lens on the launch side and the diode detector on the opposite side are both fitted onto optical mounts with a five axes adjustability (see section 4.3). The total beam path length is 430 mm whereas the path through the reaction zone is 186 mm. The long outside beam path is required to allow translation of the substrate and to protect optical components from heat radiation from the susceptor.
5.3 Monitoring of process stability through \textit{in-situ} near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

![Diagram of laser monitoring arrangement](image)

\textbf{Figure 5.2: In-situ laser monitoring arrangement}

\subsection*{5.3.2 Measurement procedures and results}

In order to obtain a spatial concentration profile, the width of the reaction zone (41 mm) was divided into 11 measuring points with an equidistant separation of 5 mm. The outer monitoring points are in the extraction zone already as illustrated in Figure 5.1. This allows to check extraction efficiency of the system as well.

At every measurement point the laser beam was re-aligned parallel to the inlet slot. It was found that precise alignment is difficult due to limited reactor access. Hence it is possible that the beam passes through the reaction zone at a small angle. This is problematic especially in regions in the reaction zone where large HCl concentration gradients are expected, e.g. close to the inlet slot where the unreacted gas mix enters the reactor and HCl creation starts at the substrate surface.

After alignment, a new glass sample (100 mm $\times$ 100 mm) was placed in the reactor and enclosed by smaller glass plates which decrease possible edge-effects from the sharp sample edge.
5.3 Monitoring of process stability through *in-situ* near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

Two different sets of experiments have been performed. The purpose of the first set was to monitor HCl during six passes of the substrate under the coating head and to relate the resulting film thickness to the continuously measured HCl concentration at different positions in the reaction zone. In the second set the substrate was held stationary and process conditions such as gas flow rates have been varied to observe their influence on HCl concentration.

5.3.3 *In-situ* measurements with moving substrate

During standard operation of this equipment tin oxide films of around 500 nm are deposited which requires six passes of the substrate under the coating head. Common operating conditions are listed below:

<table>
<thead>
<tr>
<th>Flow rate</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 L min$^{-1}$</td>
<td>Nitrogen (through bubbler filled with MBTC precursor)</td>
</tr>
<tr>
<td>0.5 L min$^{-1}$</td>
<td>Nitrogen (for water transport from syringe injection point)</td>
</tr>
<tr>
<td>1.5 L min$^{-1}$</td>
<td>Oxygen</td>
</tr>
<tr>
<td>5.0 L min$^{-1}$</td>
<td>Nitrogen (volume balance)</td>
</tr>
<tr>
<td>3.0 cm$^3$ h$^{-1}$</td>
<td>De-ionized Water</td>
</tr>
</tbody>
</table>

**Other conditions**

- 130 °C Bubbler set temperature
- 600 °C Susceptor set temperature

One minute stabilisation time is allowed after manually switching on the gas flows. Substrate movement and monitoring is then started simultaneously.

MBTC enters the reactor below its decomposition temperature and the heat of the susceptor is required to initialize decomposition. When the susceptor moves out of the reaction zone the temperature drops suddenly and precursor decomposition is stopped. Therefore the measurements show time periods of zero HCl concentration.

5.3.3.1 Monitoring results

A typical measurement result recorded in position 3 (see Figure 5.1 for beam location) is shown in Figure 5.3. Six passes of the substrate under the coating head result in six distinct HCl detection regions. Each pass appears to be mirrored to the prior one. A steep rise/drop in concentration on one side and a slightly less
5.3 Monitoring of process stability through *in-situ* near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

steep in-/decrease on the opposed flank can be observed. Further, at the begin/end of a pass often a sharp concentration spike is observed which possibly stems from fluctuations in HCl concentration caused by the edge of the glass moving into the laminar gas flow.

In position 3, the beam is positioned to the left of the inlet slot and inside of the reaction zone. Since the substrate moves into the reaction zone from the right, the coating process starts and HCl is created first to the right of the inlet slot. Past the inlet slot, HCl is extracted through the left extraction duct also which then causes a steep increase in HCl concentration (pass 1), followed by a period of relatively constant concentration with some fluctuations and a less steep drop in concentration once the substrate has passed the beam position and the remaining HCl is extracted.

At the beginning of the second pass, the substrate enters the reaction zone from the left and passes the beam after little contact time with the reactants. Therefore the concentration builds up more gradually, reaches the same plateau as in pass one and then drops rapidly once the substrate has passed the centre region and temperature suddenly drops. This sequence is illustrated schematically in Figure 5.4.

![Figure 5.3](image_url)

**Figure 5.3:** Typical monitoring result obtained from six substrate passes. A single pass is highlighted (red). A 10 point moving average smoothing was applied.

The film thickness of the sample produced during a six pass run is determined off-line through etching of the film, followed by surface profiling.
5.3 Monitoring of process stability through in-situ near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

**Figure 5.4:** HCl concentration profile during steps of the process. Beam position 3 is indicated by ●. a) The creation of HCl begins. b) The substrate passes the slot centre and HCl is produced also on the left side. c) Substrate has passed the beam and residual HCl is extracted.

Figure 5.5 shows the concentration of HCl for all 11 points. Plots are arranged in pairs of two (e.g. 1 and 11) because of the coating head’s axis symmetry.

It can be seen that the plot for 1 and 11 shows a low absorption. Also the single passes cannot be determined clearly. This is believed to be an effect of fluctuations and dilution in the extraction. The inner duct extracts all chemistry but also draws in some air from the outside which is then mixed with the reaction gas stream.

For the following positions (2, 3, 4, 8 and 10) a relatively constant absorption of around $4 \times 10^{-4}$ can be observed. These are the positions inside the reaction zone but outside of the influences of the extraction or the impinging gas stream under the inlet slot.

Positions 5 and 7 are the closest to the inlet slot. Here it is expected to generally observe a lower concentration of HCl as unreacted gas is continuously entering through the inlet slot in only 5 mm distance from the measuring position. This fresh gas quickly displaces the HCl created and the extraction also contributes to the displacement.

The spatial profiling of the reactor was repeated and results are presented in Figure 5.6. In comparison to Figure 5.5 it can be seen that concentrations of HCl have approximately halved in this experimental set. Precursor gas flows, substrate temperature, susceptor speed and sample preparation were identical. It was concluded that
5.3 Monitoring of process stability through *in-situ* near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

for the measurements carried out in set 2 a blockage was present in the precursor feed system and that parts of the vaporised MBTC did not reach the coating head. In positions 5 and 7 a low concentration of HCl is expected (as described above) but similarly to Figure 5.5, fluctuations in the concentration can be observed.

This could be a result of an alignment issue as it is difficult to adjust the beam to run parallel to the inlet slot. A slight angle may also account for higher concentrations.

Figures 5.6 and 5.5 present all experimental data recorded. The mean film thickness of the sets is 344 nm and 571 nm respectively.

It can be seen that higher concentrations of HCl measured in set 1 are also clearly reflected in the thickness of the deposited films. This potentially allows for the detection of coating head blockages during coating runs and film thickness.
5.3 Monitoring of process stability through in-situ near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

Figure 5.5: Absorption of HCl, measured on 11 positions in the CVD reactor during six substrate passes (Set 1)
5.3 Monitoring of process stability through *in-situ* near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

**Figure 5.6:** Absorption of HCl, measured on 11 positions in the CVD reactor during six substrate passes (Set 2)
5.3 Monitoring of process stability through \textit{in-situ} near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

5.3.3.2 Correlation of film thickness to HCl gas phase concentration

The plot in Figure 5.7 presents the film thicknesses of some sample substrates from the two measured sets.

It is evident, that despite the usage of identical flowrates for all experiments, there is a variation in film thickness within and between the sets. Set 1 with a mean thickness of 575 \text{ nm} presents a standard deviation of 59 \text{ nm} and set 2 344 \text{ nm} and 32 \text{ nm} respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5_7.png}
\caption{Variation of SnO$_2$ film thickness for identical flow rates of two experimental sets. Set 1 mean 575 nm, set 2 mean 331 nm.}
\end{figure}

For further analysis the two sets of experiment are treated separately because of their difference in average thickness. It is the aim to find a correlation between the measured integrated absorption and the film thickness of the resulting films.

From the results in the previous section it is evident that the location of monitoring points has a large influence on the measured absorption. Figure 5.8 shows the plot of mean integrated absorbance at various monitoring locations. Especially in set 2 the integrated absorbance fluctuates highly around the inlet slot location (6). These locations will therefore be excluded in the attempt to correlate integrated absorption to film thickness.

Values measured at locations 3, 4, 8 and 9 are more stable and appear to be suited to match to film thickness.
5.3 Monitoring of process stability through \textit{in-situ} near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

In the next step, for now only considering set 2, the film thickness is plotted against the integrated absorbance of the corresponding films (Figure 5.9) and a linear fitting function is applied. Figure 5.10 presents the comparison of the linear fitting to all measured film thicknesses of set 2. Integration absorption can be converted to film thickness with a linear function. The conversion is in good approximation the multiplication with a fixed conversion factor. From the integrated absorbance the resulting film thickness can then be estimated within about 70 nm for most coatings. The measurements do not appear to be sensitive enough to detect small variations in film thickness.

In an industrial coating process, the concentrations of HCl are much higher and the process conditions are more consistent compared to the APCVD reactor used (Martin et al. 2007). Further, because of the increased concentration, the NIR-LAS instrument noise is reduced. In such industrial conditions this concept should allow the prediction of the resulting film thickness in a much narrower range. A limitation to this approach is that, due to the laser beam path through the whole reactor coating zone, HCl in the extraction part of the reactor is also detected. Because the
5.3 Monitoring of process stability through in-situ near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

extraction can become turbulent, there will be a certain signal noise inherent to the measurement. Therefore it is unlikely that a prediction of film thickness within few nano-metre is possible.

\[
f(x) = -16080 \cdot x + 581
\]

**Figure 5.9:** Film thickness over integrated absorbance

\[
f(x) = -16080 \cdot x + 581
\]

**Figure 5.10:** Film thickness over integrated absorbance. Linear fitting function for prediction of film thickness derived from selected monitoring points

5.3.4 In-situ measurements with stationary substrate

The purpose of this experimental set was to monitor the influence of changing flow conditions on the HCl concentration. In contrast to the first set of experiments, the substrate was held stationary and centred under the inlet slot and the number of
5.3 Monitoring of process stability through in-situ near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase measuring points was reduced. For the same operating conditions a point close to the first extraction and a point close to the inlet slot was selected. Being able to detect changes in process conditions is important for reactor control and process stability.

5.3.4.1 Variation of the bubbler flow rate

The bubbler is the precursor delivery system in the experimental setup. MBTC as precursor is the only chlorine source for production of HCl in the process. Hence variation in the precursor flow will have a direct influence on the HCl concentration.

Figure 5.11 shows a time series with varied N₂ bubbler flow rate from 1 to 0.5 L min⁻¹. At first the balance nitrogen (5 L min⁻¹) was turned on together with the oxygen (1.5 L min⁻¹) and the syringe pump (water injection). In this initial phase, the bubbler was bypassed but HCl was still detected. This is an effect of precursor deposits in the pipework and the coating head. As soon as the bubbler is turned on, the HCl concentration more than doubles. In the following each flow rate was maintained for two minutes. Over the whole measurement period the concentration decreases but certain irregularities can be observed. During the 0.9 L min⁻¹ period the concentration decreased at first and rose slightly after about one minute. During the 0.8 L min⁻¹ period there is a decline in concentration where a constant level of HCl was expected. The same, but slightly less pronounced can be observed for
5.3 Monitoring of process stability through in-situ near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

0.5 L min\(^{-1}\). The non-constant concentration profile might be a result of varying amounts of precursors entering the reactor or higher fluctuations at the measurement position.

A similar series as above was recorded at position 5 (Figure 5.12). This time, however, for bubbler nitrogen flow rates down to 0.2 L min\(^{-1}\). Between the flow rate changes, the concentration is more constant and only small variations are visible. One exception is the 0.5 L min\(^{-1}\) period where a sudden concentration drop is observed. It is believed that this occurred when the water in the syringe ran out during the measurement. Subsequently, despite decreasing flow rates, the concentration reduces only moderately. This is an effect of missing water which is known to increase the deposition rate (S.-M. Lee et al. 2000). Comparing the concentration level from time 900 s onwards to the purge level at 120 s the detected HCl might also be solely a product of pipe contamination with little HCl being created from fresh precursor.

![Figure 5.12: Monitoring of HCl at position 5 during variation of the bubbler nitrogen flow rate](image)

Figure 5.13 was recorded at the symmetrical positions 9 and 3. Whilst the 1 L min\(^{-1}\) and the 0.9 L min\(^{-1}\) period are relatively constant with a minor slope upwards, the 0.8 L min\(^{-1}\) period shows a similar, but steeper, continuous drop as in Figure 5.11 in the same phase. Due to the long runtime the water ran out during this run too. This may explain the steep decrease and the little changes observed thereafter.

The last recorded bubbler flow rate variation, Figure 5.14, was recorded at position 9 and can be compared to Figures 5.11 and 5.13. It can be seen that the concentration
5.3 Monitoring of process stability through in-situ near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

Figure 5.13: Monitoring of HCl at position 3 during variation of the bubbler nitrogen flow rate

remains almost constant during the whole measurement. Also the concentration observed for the highest flow rates are about a factor of two smaller than in previous runs. The reason for this is the already earlier mentioned partial blockage of pipes or the coating head (see subsection 5.3.3).

Figure 5.14: Monitoring of HCl at position 9 during variation of the bubbler nitrogen flow rate
5.3 Monitoring of process stability through in-situ near-infrared diode laser absorption spectroscopy in the APCVD reactor gas phase

5.3.4.2 Variation of the oxygen flow rate

The influence of the oxygen content on the HCl concentration was tested as well (Figure 5.15). The usual flow rate is 1.5 L min⁻¹, which is also almost the minimum of the available flow meter. Therefore, by force of circumstance, almost only higher flow rates have been tested. In order to avoid increasing the total gas volume, the balance nitrogen was reduced by the amount of oxygen added. It is apparent that added oxygen has no influence on the creation of HCl.

![Figure 5.15: Monitoring of HCl at position 3 during variation of the oxygen flow rate](image)

5.3.4.3 HCl concentration during stepwise reactor start-up

This set of experiments was recorded to observe in more detail the influence of the various gas streams in the experimental setup. For this, balance nitrogen and/or oxygen was added prior to bubbler switch-on.

Figure 5.16 presents a time series (position 5) where all gas flows where switched on after another. Starting with the syringe transport nitrogen and the syringe little HCl is observed. Added oxygen then causes a purging effect which is enhanced with added balance nitrogen. Once the bubbler nitrogen is switched on it takes about 20 s for the HCl to reach a constant level.

A similar experiment on beam position 4 is presented in Figure 5.17. Here the gases have been switched on in a different order. Comparing the two plots, it can be seen that with all other gas flows active, it takes again about 20 s after the bubbler has
5.4 Combination of infrared grating absorption and near infrared laser absorption spectroscopy for in-line and in-situ process monitoring and control

been switched on for the concentration to stabilise. It has to be noted that (4) was recorded on a day where generally less HCl was observed. This might explain why the step in concentration is less pronounced.

Figure 5.16: Monitoring of HCl at position (5) during reactor start-up

Figure 5.17: Monitoring of HCl at position (4) during reactor start-up

5.4 Combination of infrared grating absorption and near infrared laser absorption spectroscopy for in-line and in-situ process monitoring and control

The mid-infrared grating absorption spectrometer (IR-GAS) introduced in section 4.5 was connected to the reactor after the bubbler to monitor the MBTC concentration
5.4 Combination of infrared grating absorption and near infrared laser absorption spectroscopy for in-line and in-situ process monitoring and control

entering the reactor. Simultaneous measurements with the in-situ laser absorption system (NIR-LAS) were carried out to monitor the concentration of HCl in the reaction zone at multiple points. The setup with both instruments in place on the coating system is depicted in Figure 5.18 and the corresponding schematic in Figure 5.19.

At first measurements were carried out using a stable coating system. In the next step system parameters influencing the efficiency of the coating process were changed. Parameters were chosen such that they represent realistic scenarios occurring on industrial coating systems (Table 5.1).

Figure 5.18: The near infrared diode laser absorption system (NIR-LAS) and infrared grating spectrometer (IR-GAS) installed on the APCVD coating system
5.4 Combination of infrared grating absorption and near infrared laser absorption spectroscopy for in-line and in-situ process monitoring and control

Figure 5.19: Schematic of the IR-GAS and NIR-LAS setup on the coating system

Table 5.1: Variable coating parameters

<table>
<thead>
<tr>
<th>Parameter variation</th>
<th>Possible scenario at industrial coating system causing similar variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regulation of the bubbler by pass valve</td>
<td>Blockages in gas or precursor supply</td>
</tr>
<tr>
<td>Variation of the bubbler flow rate</td>
<td>Partial blockages in pipes or coating head</td>
</tr>
<tr>
<td>Bubbler temperature</td>
<td>Precursor concentration variation (Bubbler fill level/ evaporator)</td>
</tr>
</tbody>
</table>

5.4.1 Simulation of blockages through by-passing of the bubbler

The nitrogen gas stream through the bubbler can be fully or completely diverted through a by-pass (Figure 5.19). This rapidly reduces the concentration of MBTC in the gas mixture which is a similar condition as blockages or problems in the precursor delivery system of an APCVD coating system.

The sample cell of the IR-GAS system is purged by the nitrogen stream and the NIR-LAS system is also expected to detect the reduced MBTC concentration as less HCl is produced in the chemical reactions under the coating head.

Rapid opening and closing of the by-pass valve is detected by the IR-GAS system with a delay of 1 to 2 s due to the length of the tubing between bubbler and sample.
5.4 Combination of infrared grating absorption and near infrared laser absorption spectroscopy for in-line and in-situ process monitoring and control

cell. It appears that short opening/closing cycles have little but visible effect on the HCl concentration in the reactor. This is probably due to the several meters of tubing between bubbler and coating head and turbulent mixing effects in the pipework (Figure 5.20). Prolonged by-pass times are also clearly visible with the laser system (250 to 300 s).

![Figure 5.20: Simultaneous monitoring with the IR-GAS and NIR-LAS system. The NIR-LAS system recorded HCl at two beams positions to the left and right of the inlet slot, the IR-GAS instrument MBTC in the reactor feed](image)

5.4.2 Simulation of blockages by stopping the bubbler feed

Over time impurities in the precursor can build up in the pipework to a point were the precursor flow stops. This was observed for example after overnight shutdowns of the coating system and prior usage over the duration of a working day. To simulate such a condition the flow of nitrogen through the precursor was fully stopped. In those cases the flow through the IR-GAS sample cell stops and due to the stagnant gas in the cell the system measures a constant concentration. The NIR-LAS system however almost instantaneously detects the depletion of MBTC and hence reduced HCl in the system (Figure 5.21).

Compared to the previous experiment this means that the pipes from the bubbler to the mixing point with the other reaction gases was already highly contaminated. Because even though the bubbler was bypassed, the nitrogen flowing through the
5.4 Combination of infrared grating absorption and near infrared laser absorption spectroscopy for in-line and in-situ process monitoring and control

pipes behind the bubbler contained enough MBTC to supply the reaction for a certain time (20 to 30 s).

Figure 5.21: Simulation of a complete blockage by stopping the flow through the bubbler. The NIR-LAS instrument measured HCl, the IR-GAS instrument MBTC in the reactor feed

5.4.3 Concentration variation through temperature variations in the bubbler

Bubbler systems are commonly heated in oil-bath, hotplates or heating coils. From the Clausius-Clapeyron equation (see section 4.5) it is known that the vapour pressure and hence the concentration of MBTC is strongly temperature dependent. A drift in temperature of the bubbler system over time e.g. due to failure of the heating system can lead to undesired MBTC concentrations in the coater.

To test this condition the bubbler temperature was varied from 120 to 130 °C. This narrow temperature range was chosen because it takes several hours for the bubbler to reach a stable temperature (hotplate heated) and because the condensation and decomposition in the pipework was to be avoided.

Figure 5.22 shows the result of the IR-GAS instrument in comparison to the concentrations calculated by the Clausius-Clapeyron equation presented earlier. The plot proves that the detectivity of the instrument is sufficient to detect small variations in MBTC concentration caused by small variations of temperature. It also has to be noted that towards lower temperature the measurement diverts from the
Clausius-Clapeyron equation which means that at those temperatures the vapour in the bubbler may not be saturated anymore. At 130°C bubbler temperature the measured and calculated concentration are practically identical. The NIR-LAS system showed no change in concentration for such small temperature variations.

![Graph showing variation of bubbler temperature](image)

**Figure 5.22:** Variation of the bubbler temperature monitored by the IR-GAS system and compared to the Clausius-Clapeyron equation (van Mol 2003)

### 5.5 Summary

Two optical monitoring instruments have been used to monitor the APCVD process stability and progress. The near-infrared diode laser absorption instrument (NIR-LAS) has the ability to monitor the concentration of HCl in the reaction zone spatially. Further it is shown that the instrument is sensitive to changes in process conditions such as changing flow rates of the precursor gases. In addition it is shown that the HCl concentration can be related to the thin film thickness if the laser system is positioned in the coating zone such that the signal is the most stable. For the reaction system used these monitoring points are located past the half-width of the coating zone.

The mid-infrared grating absorption spectrometer (IR-GAS) operated in-line in the precursor feed to the reactor. It monitors the concentration of the unreacted
MBTC precursor. The instrument is sensitive to changes in precursors concentration introduced through variation of the MBTC vapour pressure in the bubbler.

Simultaneous monitoring with both instruments demonstrated that, when used together, these instruments detect common faults such as depleting precursor supply and blockages in the coating system. The IR-GAS instrument has the ability to detect pipe blockages, whereas the NIR-LAS instrument has the ability to detect blockages in the coating head.
6 Thermal decomposition pathway of the Monobutyl tin tri-chloride precursor

6.1 Introduction

MBTC is a common precursor used for the deposition of tin oxide. Despite its common use, little is known about the chemical reaction mechanism in both the gas phase and at the surface. Whilst the deposition rate and crystal structure was observed under a wide range of process conditions (temperature, addition of water) by several authors (see section 2.4), no study exists that examines the gas phase composition in the reaction zone for different process conditions. The discovery of the short-lived tin containing intermediate that initiates the tin oxide growth would facilitate the development of chemical reaction models for simulation. Such simulations use simplified chemical models but it is reported that those require calibration through experimental studies (see section 2.6). With the knowledge of the molecular structure of key intermediates an enhanced model can be developed that reduces the number of assumptions and simplifications made and hence provide a more generic mechanism that can be used in design of new APCVD reactor systems.

As described in section 3.2, MBTC presents absorption bands in the mid infrared region of light and therefore FTIR spectrometry can be used to monitor precursor decomposition and the formation of further species.

6.2 Comparison of novel mid-infrared fibre optic cable and conventional mirror arrangements for in-situ FTIR monitoring in APCVD reactors

APCVD reactors are commonly not well accessible because metal shielding is used around to the coating head to protect the coating zone from disturbances (air turbulence) from the surrounding atmosphere. As mentioned previously (chapter 5), the distance between coating head and substrate is in the range of a few millimetres, making optical monitoring on such systems difficult.
6.2 Comparison of novel mid-infrared fibre optic cable and conventional mirror arrangements for in-situ FTIR monitoring in APCVD reactors

FTIR spectrometers are usually not built for in-situ process monitoring as most instruments only have a sample compartment within the instrument. Some FTIRs such as the here used Bruker Equinox 55, however, do have the capability to externalize the IR beam which is then focused onto an external detector connected to the instrument.

Conventionally mirror arrangements such as periscopes are used to redirect the beam to the desired position. Recently novel polycrystalline fibre optic cables became available that transmit infrared light in the region of 500 to 2500 cm\(^{-1}\) (Figure 6.1). From the graph it is evident, however, that the transmission losses are 40% and higher and no light is transmitted beyond about 3000 cm\(^{-1}\). This limits the use of such a fibre for in-situ gas analysis and a benchmark against a conventional mirror arrangement is required.

![Transmission spectra of the Fibre Photonics Ltd. PIR 900/1000 fibre in the mid-infrared (provided by Fibre Photonics Ltd.)](image)

**Figure 6.1:** Transmission spectra of the Fibre Photonics Ltd. PIR 900/1000 fibre in the mid-infrared (provided by Fibre Photonics Ltd.)

Light exiting the FTIR interferometer is focused into the fibre through an off-axis parabolic mirror. At the end of the fibre optic cable is a lens from which a parallel light beam is directed to an external detector. The advantage of such a fibre optic based monitoring is that the FTIR instrument can be kept outside of the reactor environment, protecting the instrument from process heat and potentially corrosive reaction gases.

In the APCVD reaction system used here, the coating head is located above the height of the workbench of the FTIR instrument. To redirect the FTIR beam to the
6.2 Comparison of novel mid-infrared fibre optic cable and conventional mirror arrangements for in-situ FTIR monitoring in APCVD reactors
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cating head using mirrors, a periscope has to be used. The periscope is built from two planar gold mirrors, with 50 mm in diameter (Figure 6.2).

![Diagram of FTIR measurement setup](image)

**Figure 6.2:** Comparison of the in-situ absorption monitoring arrangement using a polycrystalline infrared fibre and a mirror periscope

For the evaluation of fibre and periscope, spectra of air at atmospheric temperature were recorded whereas the path length of the open beam for both arrangements was identical. The relative spectral noise level of the two approaches is then the decisive factor in regards to which technique is used in further work.

The plot of two transmission spectra shows that the spectrum recorded with the polycrystalline fibre presents a higher noise level (Figure 6.3). This is mainly attributed to the generally weaker signal and to losses in the fibre coupling, the fibre itself and the lens. The lens does not provide a fully parallel light output and light diverges with a 5° angle from the optical axis. This may be tolerable in short-distance applications but leads to further loss in light intensity received by the detector. In addition, a periodic wave appears to be superimposed on the spectrum. It is not clear what the origin of this disturbance is. FTIR instrument and detector are located on different work benches which may introduce some noise due to vibration, but the periscope arrangement appears not suffer from these noise patterns.
6.3 Monitoring the decomposition of MBTC \textit{in-situ}

It is concluded that the novel polycrystalline infrared fibre is not suited for the application it is intended for. An open infrared light beam path of about 50 cm is required for successful installation on the APCVD reactor, but at this distance the transmitted light intensity is too low which leads to high noise levels. The periscope assembly proved to provide a sufficient signal strength and comparable low noise level and will therefore be used in further experiments.

6.3 Monitoring the decomposition of MBTC \textit{in-situ} on a moving substrate coating system

In this set of experiments the gas phase of an APCVD coating system with MBTC chemistry was monitored \textit{in-situ} with a FTIR spectrometer. The purpose of these experiments was to explore the possibility of \textit{in-situ} FTIR monitoring in an existing coating system with limited optical access and the monitoring and quantification of decomposition products during substrate coating.

The FTIR instrument was set up in a double path arrangement, where the infrared beam from the instrument goes through the reactor coating zone, reflects on a planar mirror back through the coating zone onto the detector. This arrangement has two
advantages over a single light pass through the coating zone. Firstly, the path length is doubled which, due to the exponential character of the Beer-Lambert law, almost triples the absorption and secondly the cryogenic detector can be kept outside of the reactor hot zone, leading to longer runtimes.

As described in section 4.2, the common gap distance between substrate and coating head during deposition is 2 mm. It was found that a sufficient signal to noise ratio for the resulting FTIR spectra could only be obtained with a gap of 7 mm. This alters the deposition characteristics as the temperature gradient from heated substrate to coating head changes. Lower temperatures at the precursor entry point to the coating zone will maintain MBTC intact for longer before sufficient thermal energy is available for decomposition closer to the substrate surface.

Further, an uncertainty of overall path length of the infrared beam is introduced as it is difficult to measure the exact beam position throughout the coating zone due to limited spatial access.

A periscope arrangement was used to raise the infrared beam from the instrument to coating head height. The adjustability of the planar mirrors was also used for alignment of the system. The detector was mounted outside of the FTIR instrument on beam height to provide the shortest beam path possible which minimizes optical losses and the number of optical components in the setup.

![Schematic setup](image)

**Figure 6.4:** Setup of the FTIR spectrometer for in-situ measurements in the gas phase. Gap height between reactor head and substrate 7 mm.
6.3 Monitoring the decomposition of MBTC in-situ

6.3.1 Experimental procedure

Three sets of experiments were conducted to investigate the influence of one process parameter whilst keeping others constant. As explained in section 4.2, the amount of precursor going into the system is controlled by the vapour pressure of MBTC in the bubbler and by the flow rate of the carrier gas through the bubbler. First the bubbler flow rate was varied in three steps: 0.2 L min\(^{-1}\), 0.5 L min\(^{-1}\) and 1.0 L min\(^{-1}\) whilst maintaining a constant bubbler set temperature (130°C) along with constant oxygen flow (1.5 L min\(^{-1}\)), water flow 3.57 cm\(^3\) h\(^{-1}\) and balance nitrogen flow (5 L min\(^{-1}\)). The standard flow rate of nitrogen through the bubbler used in production is 0.5 L min\(^{-1}\) (empirical value).

Secondly the bubbler temperature was varied by adjusting the hot plate the bubbler sits on to 135°C, 165°C and 175°C. In this case the lowest temperature is used in production, which is again derived empirically by the operators. Lowering the temperature below 130°C was avoided because of possible condensation.

For the substrate temperature it is known that at 600°C the reaction operates at the mass transfer limit and therefore this is the standard set temperature in the process. Spectra were recorded also with a much lower temperature of 500°C and at the maximum temperature allowed by the heating elements in the susceptor of 620°C.

For each experimental setpoint a number of FTIR spectra were recorded in the range of 500 to 4500 cm\(^{-1}\), mostly at a resolution of 1.0 cm\(^{-1}\). Some spectra were recorded at 0.5 cm\(^{-1}\) also. It was attempted to record every spectrum after an identical waiting time. Due to several meters of pipework in the system, a minimum waiting time of 60 s is necessary to let the concentrations of chemicals in the reaction zone stabilize.

Prior to recording a spectra, the system was purged with nitrogen. It was found that after a prolonged purge cycle > 10 min a small amount of precursor still enters the reaction zone. Presumably this is caused by deposits of precursor in the pipes due to partial condensation caused by inadequate heating of the pipes at points in the system. Also the impurities contained in the MBTC precursor build up in the pipelines over time and may release small amounts of MBTC uncontrollably.
6.3 Monitoring the decomposition of MBTC in-situ

6.3.2 Results

A typical spectra recorded with a resolution of $1\text{ cm}^{-1}$ is shown in Figure 6.5. MBTC has a strong absorption feature at around $3000\text{ cm}^{-1}$. The fine lines that are superimposed onto the broad MBTC absorption feature belong to HCl which absorbs in the same spectral region. Further, weaker absorption of MBTC can be found in the fingerprint region of the spectra at $700$ to $1500\text{ cm}^{-1}$. If water is added to the process, large absorption bands of water can also be seen. Due to the open beam path optical arrangement, the water and $\text{CO}_2$ content may vary because of atmospheric effects.

It was found that the MBTC absorption in the fingerprint region was only visible for high MBTC inlet concentrations but not at standard operating conditions. Also no further decomposition products have been observed. It is assumed that possible MBTC decomposition products can only be found in a boundary layer close to the hot surface where they must be consumed instantaneously in a surface reaction. HCl as a reaction product, however, diffuses into the bulk gas phase and therefore is detected.
6.4 Identification of decomposition species through thermal decomposition of MBTC

It was found that it is difficult to obtain high resolution, low noise FTIR spectra of the MBTC decomposition in an in-situ APCVD reactor. Especially the intensity of the peaks in the fingerprint region of the MBTC precursor were similar to the noise magnitude in the spectrum because of low precursor concentrations in the gas phase. For this reason an experiment was designed that allows the decomposition of tin oxide precursors over a wide temperature range with subsequent optical monitoring of the resulting decomposition species. The experimental setup is described in detail in section 4.4 and a picture of the setup is presented in Figure 6.6.

6.4.1 Experimental procedure

In a standard mode of operation, the nitrogen flow through the bubbler was set to $400 \text{ml min}^{-1}$ with a bubbler temperature of 60 to 70°C. The oven was operated
from 200 to 760 °C and optionally nitrogen or oxygen with a flow rate of 40 ml min⁻¹ was added. If water was added (0.16 to 0.81 mL h⁻¹), it was transported either by nitrogen or oxygen to the mixing point with the MBTC feed.

After passing through the oven, the gas mixture cooled down to 150 to 170 °C at the optical cell.

The system was purged with pure nitrogen prior of adding the MBTC precursor. At the end of a purge cycle and once temperatures had stabilized, a background spectrum was recorded by the FTIR spectrometer. Typically 30 scans where recorded at a spectral resolution of 0.5 cm⁻¹ for the background and the signal.

Gas in the oven can be heated to a wide range of temperatures, whereas the rest of the system is maintained at a constant temperature of 130 °C to avoid condensation. A range of 177 to 720 °C was used for the oven temperature. It is reported that MBTC starts decomposing at around 450 °C (Chae 2004). At temperatures below the decomposition temperatures the spectrum should therefore show pure MBTC. Slight
variations in peak width and intensity due to broadening effects with temperature are expected.

The vapour pressure in the bubbler and the flow of nitrogen through the bubbler was maintained constant for each set of experiments.

To record a signal spectrum, the bubbler was opened and a 30 scans averaged spectrum was recorded after a 30 s stabilization time. Following this initial spectrum, further spectra with oxygen and/or water were recorded, followed by interim purge cycles, a final purge cycle and heating/cooling to another oven temperature.

It was attempted to maintain a constant timing between opening the bubbler and recording the signal spectrum in order to ensure comparable conditions. Due to pipe blockages and cleaning of the optical windows, some scans had to be repeated on consecutive experiments which led to slight changes in the experimental conditions.

6.4.2 Results

6.4.2.1 Thermal decomposition of MBTC

A typical spectrum of MBTC can be seen in Figure 6.7. The C–H vibrations show a dominant peak just below 3000 cm\(^{-1}\) and from 500 to 1500 cm\(^{-1}\) the fingerprint region can be seen. Because it is an open beam experiment, traces of water and CO\(_2\) are visible at 1500 cm\(^{-1}\), 3800 cm\(^{-1}\) and 2300 cm\(^{-1}\) respectively because of slight changes in humidity and carbon dioxide content in air between the background and the signal spectrum.

Up to a temperature of 300 °C no change in the spectrum was observed but at 321 °C traces of HCl (hydrogen chloride) and C\(_2\)H\(_4\) (ethene) start to appear (Figure 6.8). Chae, Houf, McDaniel and Allendorf notes that the breakage of the carbon chain C\(_4\)H\(_9\) from the tin-chlorine radical SnCl\(_3\) initiates the MBTC decomposition (Chae 2006). This will alter the infrared spectrum, but at lower temperatures the amount of decomposed MBTC appears to be below detection limit and the fingerprint and C–H vibration peaks are unchanged. With rising temperature however, the hydrogen chloride and ethene concentrations rise and at around 430 °C the C–H peak at 2960 cm\(^{-1}\) underwent a clear change in shape due to decomposition of MBTC. The formed C\(_4\)H\(_9\) then decomposes further into shorter and more stable carbon chain molecules due to the exposure to high thermal energy. Furthermore, methane (CH\(_4\)
can also be identified through a peak at 1306 cm\(^{-1}\). Besides increasing concentration of the decomposition products mentioned, no further species appear to be created. The highest temperature measured was 628 °C.

At 1165 cm\(^{-1}\) an unobstructed absorption band was found with a fading peak as decomposition progresses. This peak can be used to identify MBTC and to measure the progress of decomposition. It can be seen in Figure 6.9 that starting from 300 °C the peak decays towards higher temperatures. At 403 °C the peak is still present but disappears at 420 °C. This is analogous to the previously observed change in the peak shape of the C–H peak at 2960 cm\(^{-1}\).

As mentioned above, after the MBTC molecule begins to decompose, it breaks into various carbon chain molecules. To clearly identify a molecule from an infrared spectrum, it must not be overlaid by another species at a minimum of one of its absorption bands. HCl and C\(_2\)H\(_2\) are identifiable through their sharp absorption

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**Figure 6.7:** Spectrum of MBTC, Bubbler temperature 100.9 °C, Gas temperature in measuring cell 149.3 °C, resolution 0.5 cm\(^{-1}\) (see Figure B.2 for page size version)
peaks even though they share absorption bands with other molecules. It is more complex to identify the carbon chain molecules as they share almost all strong absorption bands due to group vibrations. Nevertheless, some evidence can be found for identification (Figure 6.10).

It is conceivable that after the \( \text{C}_4\text{H}_9 \) formation butane (\( \text{C}_4\text{H}_{10} \)) is produced through bonding with a free hydrogen atom although no free spectral band was found for peaks of butane. Free hydrogen molecules might form through abstraction from the \( \text{C}_4\text{H}_9 \) and subsequent formation of 1- and 2-butene \( \text{C}_4\text{H}_8 \). Butene is industrially formed by the dimerization of ethene (\( \text{C}_2\text{H}_4 \)). Therefore it appears logical that when provided with sufficient thermal energy the pathway is reversed and butene decomposes to ethene. 1-butene was identified through its free absorption band at \( 1650 \text{ cm}^{-1} \) and 2-butene through the absorption feature at \( 670 \text{ cm}^{-1} \). Although this
Figure 6.9: Absorption peak of MBTC in the fingerprint region decays as decomposition progresses.

band is overlayed by carbon dioxide, the broad characteristic of the 2-butene feature in contrast to the sharp CO$_2$ peak is sufficient for identification.

In the process of butene decomposition, the formation of methane (CH$_4$) was also reported and small quantities are found in the spectrum with a free peak at 1300 cm$^{-1}$ (Kebarle 1957).

It appears that small quantities of 1,3-butadiene (C$_4$H$_6$) are also produced. This might occur through further abstraction of two hydrogen atoms from butene. At 1590 cm$^{-1}$ the absorption of 1,3-butadiene contributes to the right wing of a combination absorption feature with 1-butene.
6.4 Decomposition species of MBTC

Figure 6.10: Decomposition of MBTC at $600^\circ$C. Monitoring temperature $174^\circ$C. Simulated spectra are calculated with HITRAN data, all other spectra are from the PNNL database of standard spectra at $50^\circ$C.
Free hydrogen molecules are also likely to form hydrogen chloride with chlorine atoms abstracted from the SnCl$_3$ radical. Hydrogen chloride is present in the 3100 to 2600 cm$^{-1}$ range with the strongest peaks around 2800 cm$^{-1}$. SnCl$_2$ is a stable solid in form of white powder and was found in the pipes that run through the oven during cleaning of the experiment. It is therefore likely that free chlorine atoms are available which could bond with hydrogen to form hydrogen chloride.

Through the additive character of the Beer-Lambert law, the absorption of all components can be summed to form an overall spectrum composed of each individual spectrum.

$$A_{\text{overall}} = \sum_{i=1}^{n} A_i$$

$$= \sum_{i=1}^{n} \epsilon_i \cdot c_i \cdot l$$

For comparison, the measured spectrum of the MBTC decomposition is plotted together with the sum of absorption of all components discussed above. It can be seen that the two spectra match closely (Figure 6.11).

It has to be noted however, that the maximum temperature of standards spectra from the PNNL database is 50 °C and that the monitoring temperature was 174 °C (Sharpe et al. 2004). With the temperature dependency of the linestrength ($S(T)$) there is an inherited error due to the temperature difference between the measured and standard spectra. Whilst the difference in line intensities over that observed temperature range has little influence on the identification of species, there exists an uncertainty regarding the absolute concentrations of the species.
6.4 Decomposition species of MBTC

Figure 6.11: Decomposition of MBTC at 600 °C and summation of all identified decomposition species (see Figure B.4 for page size version)

6.4.2.2 Thermal decomposition of MBTC and oxygen

In the deposition process, oxygen is added to the precursor gas mixture to form SnO$_2$ on the substrate. Chae, Houf, McDaniel and Allendorf postulated a mechanism where a tin chlorine intermediate reacts with surface absorbed oxygen to tin oxide (Chae 2006). In the previous section it was shown that MBTC decomposes in gas phase into several species including stable carbon chains of various length whose formation is driven by various carbon containing radicals. Figure 6.12 shows that, provided with sufficient thermal energy and in the presence of oxygen, those gas phase radicals bond with oxygen and therefore the decomposition process is altered. Formaldehyde (CH$_2$O) and carbon monoxide (CO) are newly formed species in the presence of oxygen. Carbon monoxide (CO) is produced in large quantities as well.
At temperatures above deposition temperature (767 °C), all carbon chains with more than two carbon molecules as well as Formaldehyde appear to be destroyed through thermal decomposition. Ethene, carbon monoxide and -dioxide and hydrogen chloride remain visible in the spectrum.

Figure 6.12: Decomposition of MBTC with oxygen over a temperature range of 177 to 767 °C (see Figure B.5 for page size version)

As for the decomposition of pure MBTC, with rising temperature hydrogen chloride and ethene are visible first from about 300 °C upwards. Carbon monoxide creation begins at approximately 430 °C simultaneously with an increase in carbon dioxide concentration. As carbon dioxide is also present in atmosphere and varies during the measurement duration, its concentration can only be estimated, but towards high temperatures it is evident that the concentration of CO₂ by far exceeds the atmospheric variations and therefore must be produced in the reaction.
Analogous to the decomposition of pure MBTC, individual molecules are identified through overlaying component standard spectra with measured spectra. Figure 6.13 presents the spectrum recorded at the common deposition temperature of 600°C.

Ethene and formaldehyde are identified from the left and right wing of the peak at 3000 cm\(^{-1}\). Ethene also has a unique sharp absorption feature at 950 cm\(^{-1}\) which, however, is shared with broader absorption bands of 1,3-Butadiene, 1-Butene and 2-Butene.

Besides the above mentioned absorption of Formaldehyde at 2800 cm\(^{-1}\) which solely defines the right wing of the C-H vibration feature, there is a second feature in the 1745 cm\(^{-1}\) region. This feature, however, is in the absorption region of the atmospheric water and therefore difficult to use for quantification.

Methane can be found in small quantities at 3000 cm\(^{-1}\) and 1306 cm\(^{-1}\) whereas both features share absorption features with other components. Through their unique characteristic of sharp absorption features, however, Methane as well as Hydrogen chloride can be quantified.

As for the carbon chains, 1,3-Butadiene, 1- and 2-Butene can only be identified by looking at the whole spectrum shape, rather than at individual peaks. 1-Butene is the only C-H containing molecule that has a strong absorption in the centre of the 3000 cm\(^{-1}\) peak. 1,3-Butadiene contributes to the left wing of the 3000 cm\(^{-1}\) feature as well as to the right wing of the 950 cm\(^{-1}\) feature. 2-Butene is more complicated to identify, but its presence together with 1-Butene is likely and contributes to the overall peak shape once all components are added together (Figure 6.14).

The summation spectrum of the individual components again matched well with the experiment. From 600 to 750 cm\(^{-1}\) however the line intensities of CO\(_2\) are lower for the summation spectrum which in this wavenumber range is based on HITRAN data (Rothman et al. 2009). Individual peaks of both spectra are however at the same wavenumber and therefore it is believed that no other species contributes to the absorption in this range and that the discrepancy is solely related to the HITRAN data and instrument effects.
Figure 6.13: Decomposition of MBTC with oxygen at 600°C. Monitoring temperature 174°C. Simulated spectra are calculated with HITRAN data, all other spectra are from the PNNL database of standard spectra at 50°C.
6.4 Decomposition species of MBTC

Figure 6.14: Measured spectra of the thermal decomposition of MBTC and oxygen at 600 °C with overlayed summation spectrum of individually identified components (see Figure B.6 for page size version)
6.4.2.3 Thermal decomposition of MBTC, oxygen and water

The presence of water is known to accelerate the tin oxide deposition (Allendorf, Houl et al. 2006). It is however not clear if water is a surface absorbed species or if water influences the gas phase chemistry such as oxygen does. Chae, Houf, McDaniel and Allendorf postulated a mechanism for simulation in which water forms a complex with the MBTC (Chae 2006). Water was added to the MBTC and oxygen mixture through a syringe housed in a syringe pump. In the FTIR in-situ experiments on the APCVD reactor system (see Figure 6.5), adding water appeared not to alter the decomposition process in a way that new gaseous stable species were observed. This is confirmed in this more controlled experiment. Due to the water present in atmosphere and the open beam arrangement, quantifying the water content consumed in the reaction system is not possible. It is concluded that water is either participating in the surface reaction only and therefore does not form stable gaseous species, or that the molecule formed with water in gas phase is not observable with the FTIR spectrometer. Either because the molecule is short-lived or absorbs outside of the FTIR wavelength range.

6.5 Possible reaction pathway of tin oxide deposition from MBTC, oxygen and water

From the stable gaseous species observed in FTIR spectroscopy a possible overall reaction mechanism is postulated. The initial reaction is a $\beta$-elimination reaction which forms butene and a tin-chlorine radical. The tin-chlorine radical then diffuses to the substrate surface where it reacts with surface adsorbed oxygen to solid tin oxide and chlorine desorbs from the surface and diffuses back into the bulk gas stream. The chlorine can then form HCl with free hydrogen atoms. Butene decomposes to 1,3-butadiene while hydrogen is released. Two possible pathways emerge for the decomposition of 1,3-butadiene, one of which is the complete oxidation, resulting in carbon monoxide and water formation. Oxygen is supplied in excess and should not limit the reaction. A partial oxidation of 1,3-butadiene might also be possible. This could lead to the formation of the observed species formaldehyde, methane and carbon monoxide. Water is known to accelerate the deposition process, but the spectral data did not show an alteration of stable species formation in the gas phase in comparison to the reaction of MBTC and oxygen (S.-M. Lee et al. 2000). It is
concluded that water or its dissociation products are involved in surface reactions (which can not be observed with gas phase FTIR monitoring) which facilitate the film growth.

- $\beta$-elimination reaction of MBTC (Knyazev et al. 1994)
  
  \[ C_4H_9SnCl_3 \rightarrow C_4H_8 + H + SnCl_3 \]

- \[ C_4H_8 \rightarrow C_4H_6 + H_2 \] (Aston et al. 1946)

- \[ C_4H_8 \rightarrow 2C_2H_4 \] (Aston et al. 1946)

- Complete oxidation of ethene (Haul 1987)
  
  \[ C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \]

- Partial oxidation of ethene (Herron et al. 1969; Haul 1987)
  
  \[ C_2H_4 + O \rightarrow CH_3 + CHO \]

- \[ O + CH_3 \rightarrow CH_2O + H \]

- \[ H + CH_3 \rightarrow CH_4 \]

- \[ O + CHO \rightarrow CO + OH \]

- \[ O + OH \rightarrow O_2 + H \]

- Dissociation of water \[ H_2O \rightarrow OH + H \]

- Film deposition
  
  \[ SnCl_3(g) + O_2(s) \rightarrow SnO_2(s) + 3Cl(g) \]

- \[ 3H + 3Cl \rightarrow 3HCl \]

6.6 Summary

The decomposition of the tin oxide precursor Mono-butyl tin-trichloride (MBTC) was investigated using FTIR absorption spectroscopy. This precursor is popular in industry because it yields high deposition rates. So far the tin containing intermediate species initiating the tin oxide growth is unknown which makes it difficult to model MBTC deposition during reactor design. It is therefore desirable to identify this intermediate.

MBTC was thermally decomposed in its pure state and in mixtures with oxygen and oxygen and water. Industrially MBTC is used with oxygen and water because water
accelerates the deposition process. The experiments show that the presence of oxygen alters the decomposition compared to that of pure MBTC and that stable gaseous species such as CO, CO$_2$ and CH$_2$O emerge in the presence of oxygen. The addition of water on the other hand appears to have no influence on the decomposition reactions. Either water is not participating in the gas phase reactions or FTIR absorption spectroscopy is unable to detect the water containing intermediates. Possible reasons are that the FTIR spectrometer is not sensitive enough to detect the short-lived intermediate or that it absorbs outside of the wavelength range of the instrument.

When MBTC begins to decompose the long C$_4$H$_9$ carbon chain is abstracted from the tin molecule and other carbon chain molecules such as 1,3-butadiene, 2-butene, 1-butane, butane and ethene are formed. It was attempted to find evidence for the presence of these species in the spectral data, but because the molecules share most vibrational bands, it is difficult to conclude the presence of some species and their quantities. Smaller molecules with narrow absorption bands have been clearly identified.

Further a peak at around 1165 cm$^{-1}$ was identified which can be used as a measure of MBTC decomposition. No other absorption band overlaps with this peak and it can be solely attributed to the MBTC molecule.

Spectral evidence for key tin intermediates in the gas phase were not found. It however certain that MBTC decomposes already in the gas phase as this is evident from the stable species emerging towards higher temperatures. Therefore the tin containing compounds must exist in the gas phase and not only in the boundary layer near the surface. Most likely the absorption bands of the tin intermediates are located outside of the FTIR spectral range or the sensitivity of the instrument is insufficient to detect such short lived species.
7 Computational Fluid Dynamics modelling of an APCVD thin film deposition reactor

7.1 Introduction

Computational modelling of CVD processes is a relatively low cost and rapid method compared to prototyping reactors based on empirical knowledge as is done routinely in the CVD industry.

The aim of CVD reactors is to achieve an even distribution of the chemical mixture across the substrate and a laminar flow profile in order to ensure a film of equal thickness across the whole substrate. CFD modelling has a large potential to optimize the flow patterns inside a CVD reactor through testing of various chemical distribution geometries or modification of existing designs. Further, CFD modelling allows the implementation of chemical reaction mechanisms to predict species concentration distributions and film growth rates. These models mostly use simplified reaction pathways because of the often unknown real elementary reaction steps and to save computational effort.

In this work the geometry of an existing APCVD reactor is used to predict the film deposition rate and chemical species distribution in the gas phase. The results are compared to those of the laser absorption monitoring of hydrogen chloride (see chapter 5). The chemical mechanism used is the one proposed by Chae, Houf, McDaniel and Allendorf, which was developed to predict growth rates only (Chae 2006). The comparison to laser absorption monitoring results will allow to evaluate the accuracy of this mechanism regarding the gas phase concentration of hydrogen chloride and a general evaluation of the quality of the gas distribution in the existing reactor.

It is common practice in the simulation of CVD reactors to model only two dimensional (2D) models to save computational effort. For this, a section at the centre of the reactor along the axis the substrate is moving on is selected. Because the flow in the reactor is laminar and the precursor distribution ideally uniform, the two dimensional model is sufficient to predict growth rates for large parts of the substrate. Towards the edges of the reactor commonly edge effects are observed which manifest themselves as films of non-uniform thickness. Edge effects are caused
by the extraction or influences from the surrounding atmosphere. These effects are however omitted in 2D models and therefore these models are not suited for the investigation and improvement of reactor designs.

Only 3D models show the distribution of the reaction gases and flow patterns in space and therewith identify potential design shortcomings. For the comparison to optical measurements a 3D model is also required because edge effects do influence the concentration of HCl measured by the instrument as the laser beam passes through the complete reactor coating zone. Therefore a model is required that consists of the full three dimensional coating zone, in order to be able to compare measurement and simulation.

Building a CFD model for APCVD deposition modelling is a multi step process as depicted in Figure 7.1. The process can be subdivided into three main segments: geometry, numerical simulation and post-processing each of which will be explained with the relevant detail in the following sections.

Figure 7.1: Schematic diagram of the suggested workflow for setting up a computational simulation for species deposition in Fluent
7.2 Model geometry and meshing

7.2.1 Model geometry

In a CFD simulation, the flow of fluids between solid objects is modelled. In CVD this is the flow of precursors through a coating head and onto the deposition surface, followed by the extraction of the gas mixture from the coating zone. The model geometry requires sufficient detail from the real geometry for accurate predictions. It is expected that results increase in accuracy if the modelling geometry represents the same complexity as the real geometry. The drawback is that complex geometries increase the computational cost (Villi et al. 2014). Often axis symmetry of objects is used to reduce the model geometry. With the assumption that no asymmetric effects are present only a fraction of the real geometry is represented in the model geometry.

It is evident from Figure 7.1 that the model building process is an iterative process requiring corrections of the geometry based on results or errors in the numerical simulation. Further, the PC hardware is a limiting factor as the model needs to be loaded into memory for simulation.

The physical dimensions of the coating head are depicted in Figure 7.2.

The geometry was created in the meshing software Gambit and is based on the dimensions from the moving substrate APCVD reactor. Figure 7.3 and Figure 7.4 show a representation of the reactor used for the 3D CFD calculations. The domain represents one quarter of the actual reactor and has two symmetry planes in X and Y- direction (green). Usage of symmetry was necessary to reduce the model size because of PC hardware limitations (16 GB memory). This simplification implies that the coating head is built fully symmetrical and that no asymmetric external forces act on the coating head.

The reduced model’s main parts are a fluid inlet slot which is modelled as a vertical duct of half of the actual slot width and length and two vertical extraction ducts (red), a substrate surface and the surrounding atmosphere (blue).

The surrounding atmosphere is modelled with a volume around the reactor and a pressure inlet that allows for an air inlet flow at atmospheric pressure. The substrate is represented by a cut-out from the domain, leaving a 2 mm gap to the reactor wall (yellow).
7.2 Model geometry and meshing

![Diagram of APCVD reactor coating head]

**Figure 7.2:** APCVD reactor coating head. a) Top view, b) Side view. Dimensions in mm. Substrate position is illustrated through blue outline in the top view.

The model is built on the assumption that the precursor gas mixture enters the fluid domain ideally mixed and laminar. Thus the inlet duct can be modelled shorter compared to the actual reactor and further, modelling of the laminarizer is
not necessary. Reducing the geometry saves computational effort significantly (see subsection 7.2.2).

Under the same premise the extraction ducts were designed. As species concentrations are of little interest in the top of the extraction ducts, reducing of the duct length is possible. The ducts need to be high enough, however, to allow velocity vectors to align in flow direction for convergence (see section 7.4).

**Figure 7.3:** Side view of the reactor geometry. Symmetry planes in green, pressure outlets in red, pressure inlets in blue and general walls in yellow

**Figure 7.4:** Top view of the reactor geometry
7.2 Model geometry and meshing

7.2.2 Meshing

7.2.2.1 Meshing fundamentals

The simulation used is of the finite volume type. Finite volume simulations evaluate the set of partial differential equations introduced in section 3.6 at each mesh cell centroid. Figure 7.5 shows a mesh in two dimensional space. A number of cells with width $\Delta x$ and height $\Delta y$ form a mesh. The results of the differential equations solved for the central cell C (red) and its neighbouring cells are connected through points at their interface (blue). To calculate the interface values in the simplest case, a linear gradient between to cell centres is assumed. This means that if in the physical world large gradients of temperature, concentration or velocity are present in a specific volume, mesh cells need to be much smaller than that volume in order to resolve the observed gradient. A crude mesh will inaccurately represent real world effects whilst a fine mesh demands computational time. There is an obvious trade-off between accuracy of the solution and computation time. Practically a mesh is constructed so that it is dense in regions of interest and coarse elsewhere.

From the trade-off between accuracy and cell size (which translates to computational time) it is evident that a risk exists that the model solution inherits a mesh dependency. Checking the independence of the solution to the mesh is thus important. In such a check a denser mesh is created using the same model geometry and conditions compared to a coarser mesh for which a numerical solution exists. If the solution of that simulation is identical to the previous, it is said to be independent of the solution. In cases where the base model already occupies all physical computer memory, an independence check is not easily performed and sometimes impossible because of hardware limitations.

7.2.2.2 Meshing of the APCVD reactor model

In meshing a physical object one has the option to create cells from different geometric primitives such as hexahedra or tetrahedra. As a tetrahedra occupies less space compared to a hexahedral cell of identical edge length, the cell count in the model increases if such elements are used. The use of such elements is however necessary e.g. in modelling rounded corners.
In the APCVD reactor model, as it can be seen in Figure 7.4, only hexahedral cells are modelled because the reactor parts consist of right-angled elements only. This saves physical computer memory and is sufficient for the present geometry. The spacing of cells is more dense in regions where large gradients are expected. This is especially the coating zone where the gas mixture impinges on the substrate and large temperature and chemical species gradients are present as well as velocity gradients. Further away in the pressure inlet zone the grid is more coarse as this zone contains only air with no chemical reaction and a stable velocity field.

To achieve this zone separation and hence meshes of various density, the fluid domain was subdivided into larger volumes first. Interface faces were defined on faces shared by two volumes. A transition volume was defined to bridge the significant cell size variation between the atmosphere and the reactor volume. Meshing was then performed hierarchically by meshing volume edges first, followed by faces and then volumes. This allows for a fine control of the mesh structure (Figure 7.6).
7.3 Reactor chemistry

A common problem many CVD processes face, is the lack of fundamental understanding of the reactor chemistry. Often short living and growth initiating species are unknown.

For the reaction of MBTC with oxygen and water the tin containing species that diffuses to the substrate is not known and also FTIR spectroscopy (chapter 6) did not reveal this growth initiating molecule. For this reason computational simulations resort to simplified chemical reaction mechanisms of only a few reaction steps.

The mechanisms usually consists of the most abundant chemical species so that stoichiometric balance achieved. Further, most developed mechanisms focus on the simulation of the film growth rate and not both, growth rate and gas phase species concentration.
Chae, Houf, McDaniel and Allendorf developed a simplified chemical reaction mechanism for the deposition of SnO$_2$ from MBTC (Chae 2006). In this mechanism, the precursor rapidly forms a complex with water on exposure to the reactor heat. After diffusion and adsorption onto the substrate surface, this complex then undergoes a rate determining surface reaction with oxygen to form the solid film with hydrogen chloride (HCl) and ethylene (C$_2$H$_4$) as reaction by-products. The mechanism is shown below. The Arrhenius rate constants are derived from a low pressure experiment in a continuously stirred tank reactor (CSTR) and have been extrapolated to atmospheric pressure (van Mol 2003).

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Reaction</th>
<th>$A_1 = 1 \times 10^8$ a) $E_a = 4.18 \times 10^4$ b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas phase:</td>
<td>$C_4H_9SnCl_3 + H_2O \rightarrow C_4H_9SnCl_3(H_2O)$</td>
<td></td>
</tr>
<tr>
<td>Surface:</td>
<td>$C_4H_9SnCl_3(H_2O)(s) + 0.5O_2 \rightarrow SnO_2(s) + 2C_2H_4 + 3HCl$</td>
<td>$A_2 = 1.6 \times 10^4$ a) $E_a = 5.73 \times 10^4$ b)</td>
</tr>
</tbody>
</table>

a) in mol m s

b) in J mol$^{-1}$

In order to compute diffusion coefficients and viscosities from kinetic theory, Lennard-Jones input parameters are required (see subsection 3.6.2 and subsection 3.6.3). The parameters for all species used are presented in Table 7.1.

**Table 7.1:** Lennard-Jones parameters of species used in the simulations

<table>
<thead>
<tr>
<th>Species</th>
<th>Collision diameter $\sigma$ (Å)</th>
<th>Well depth $\epsilon$ (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4H_9SnCl_3$</td>
<td>5.5</td>
<td>528.07</td>
<td>M. Li et al. (2006)</td>
</tr>
<tr>
<td>$C_4H_9SnCl_3(H_2O)$</td>
<td>4.55</td>
<td>549.78</td>
<td>M. Li et al. (2006)</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>2.61</td>
<td>572.4</td>
<td>Cloutma (2000)</td>
</tr>
<tr>
<td>O$_2$</td>
<td>3.46</td>
<td>107.4</td>
<td>Cloutma (2000)</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>3.97</td>
<td>280.79</td>
<td>Cloutma (2000)</td>
</tr>
<tr>
<td>HCl</td>
<td>3.34</td>
<td>344.7</td>
<td>Cloutma (2000)</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>4.53</td>
<td>586.98</td>
<td>M. Li et al. (2006)</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.621</td>
<td>97.53</td>
<td>Cloutma (2000)</td>
</tr>
<tr>
<td>Air</td>
<td>3.71</td>
<td>78.6</td>
<td>Rosner (2012)</td>
</tr>
</tbody>
</table>

The mechanism above was used throughout all simulations, but the surface reaction rate required modification in order to match experimentally determined film thick-
nesses (see Figure 5.7). M. Li et al. also found that the rates postulated by van Mol did not match their two dimensional simulation of and on-line coating system (van Mol 2003). The growth rate controlling surface reaction required a reduction of the pre-exponential factor in the Arrhenius equation by two orders of magnitude (M. Li et al. 2006).

In this work the growth rate was adjusted as well to match experimental results. For this, a substrate was stationary coated for a defined time span, followed by a film thickness measurement. A part of the film was etched off the substrate using zinc powder and a hydrogen chloride– water solution. A surface profiler (Dectak) was then used to scan across the etched step and to determine the film thickness.

The rate of the surface reaction was then adjusted to match the experimental growth rate at the gas flow impinging point on a stationary substrate. A value of $A_r = 120$ for the surface reaction pre-exponential factor was then used. FLUENT calculates the deposition rate ($\text{kg m}^{-2}\text{s}^{-1}$) which requires division by the density of SnO$_2$ to calculate the growth rate in nm s$^{-1}$. For tin oxide crystalline material is assumed to be 6900 kg m$^{-3}$ throughout.

### 7.4 Computation

For laminar flows of incompressible fluids Fluent offers the pressure based segregated solver ((Patankar et al. 1972)). During the computational process all differential equations introduced in section 3.6 are solved sequentially for every grid cell centroid. Fluent allows, however, to select which equations are solved. When the solution process is initialized, initial values are inserted into the the differential equations. Because this initial guess often deviates from the final solution, gradients between grid cells are large during the first 10 to 20 iteration steps. In Fluent it is advisable to start by only solving the momentum equations until the residuals decrease. Following this, the energy equation can be activated which usually converges in about 5 iteration steps. The chemical reaction equations require the largest timespan in the computational process of about 300 to 500 iteration steps. It is not uncommon to observe residuals of $1 \times 10^{30}$ for chemical species in the first iterations steps. This is a result of the initialization of the species concentration based on boundary condition and the large concentration gradients in the simulation domain. If the flow field
(momentum equation) is not sufficiently stabilised at this point, the Fluent simulation algorithm interrupts.

Figure 7.7 shows the initial computation residuals. The residuals are a measure of convergence of a numerical simulation. For a computer with infinite numerical precision the residual would become zero, but workstation computers can only calculate numbers to a certain precision. This causes the residual to approach a small number (e.g. $1 \times 10^{-5}$) before they level out and no further change is observed (Fluent Inc. 2003, section 25.18.1).

![Figure 7.7: Residuals of the initial 150 iteration steps. Momentum equation is solved first, followed by the energy equation and the chemical species](image)

The Fluent segregated solver calculates scaled residuals (Fluent Inc. 2003, section 25.18.1). In laminar flow regimes velocity vectors are commonly regarded as converged if the residual approaches $1 \times 10^{-3}$. In the simulations performed in this work the extraction duct was modelled shorter than the actual reactor extraction to reduce the number of cells and the computational burden. The velocity vectors in the upward z-direction are therefore not fully aligned and because the boundary condition for
7.5 Simulation results

The velocity $\frac{\partial u}{\partial z} = 0$ does not hold, some vectors point back into the fluid domain at the outlet. Within Fluent this is reported as reversed flow. Because the outflow is far away from the reaction zone and not the region of interest, this reverse flow was tolerated along with a z-velocity residual higher than that of the x- and y-velocity.

The energy equation converges rapidly to $1 \times 10^{-5}$ which is not surprising, given that the substrate is the only source of heat in the system and the bulk material is nitrogen modelled as an ideal gas.

The formation reaction of the MBTC-water complex was excluded from the convergence criteria as convergence is difficult due to the fast reaction rate of MBTC and water directly on entering the reactor. The reaction occurs almost instantly which produces large concentration gradients between mesh cells. A higher grid density in vertical z-direction at the inlet could improve the MBTC-water complex convergence, but since the well converging surface reaction controls the deposition rate and all by-product formation, the formation reaction plays a lesser role in the convergence of the overall solution.

All other chemical species were converged at least to a residual of $1 \times 10^{-3}$. Some fluctuations of the chemical species residuals are observed mostly because of the issue of shortened exhaust ducts and some reversed flow but within margins that were regarded as acceptable.

The simulation was stopped once all convergence criteria were met.

7.5 Simulation results

From the chemical model described above it is known that the MBTC-water complex rapidly forms in the gas phase and is then consumed in the reaction zone. Figure 7.8 depicts the molar concentration of the radical at cross-sections of the reactor. The MBTC-water complex flows down vertically through the inlet slot at high concentration. After impinging on the substrate surface, it is consumed in the reaction zone (x-direction). At the end of the inlet slot (backmost cross-section) the complex concentration appears to be less in contrast to the centre of the reactor.

The hydrogen chloride concentration profile is very similar (Figure 7.9). Close to the symmetry plane of the reactor HCl is visible throughout the reaction area and in the first extraction stage. Further away from the centre the HCl concentration decays to
7.5 Simulation results

Figure 7.8: Molar concentration in kmol m$^{-3}$ of the MBTC-water complex with overlayed numerical mesh

a point where it is not visible in coating zone and in the extraction. The overlayed velocity vectors along the symmetry plane show a flow field well aligned in parallel with the coating head and the substrate.

From the results in Figure 7.8 and Figure 7.9 is becomes evident that a three dimensional simulation is necessary in order to evaluate flow dynamics and species distribution in a reactor. In a 2D simulation along the symmetry axis the changing concentration distribution of the water complex and hydrogen chloride towards the back of the coating zone would have remained undetected. This would lead to the assumption that the deposition rate is uniform across the substrate, where actually the reduced chemical species concentrations in some reactor parts point towards a non-uniform deposition rate and edge effects on the substrate.

Certain chemical properties are computed from kinetic theory by using the equations presented in subsection 3.6.2 and the following. The laminar diffusion coefficients, viscosity, thermal conductivity are computed from Lennard-Jones parameters whereas the thermal diffusion coefficients are computed from material properties. Because the collision integral $\Omega$ in calculation of the Lennard-Jones potential depends on the
7.5 Simulation results

Figure 7.9: Molar concentration in kmol m\(^{-3}\) of the hydrogen chloride (HCl) with overlayed velocity vectors along the symmetry plane (magnified)

dimensionless temperature \(T^*\) (see e.g. Equation 3.45) the quantities vary within the reactor. Therefore the results are presented as contour plots along the reactor symmetry axis.

Species diffusion coefficients
7.5 Simulation results

Figure 7.10: Laminar diffusion coefficients for each species computed by Fluent (Units: m$^2$/s$^{-1}$)
Species thermal diffusion coefficient  The species thermal diffusion coefficients are computed from an empirical equation (see subsection 3.6.5, Kuo (1986)).

(a) MBTC  (b) MBTC(H$_2$O)  
(c) O$_2$  (d) C$_2$H$_4$  
(e) HCl  (f) H$_2$O
7.5 Simulation results

Mixture properties, reaction rates and flow characteristics  The mixture viscosity, thermal conductivity and specific heat are calculated based on the equations presented in subsection 3.6.1. The reaction rates for both modelled reactions are calculated from the Arrhenius law (Equation 3.62). The Reynolds number is a dimensionless quantity used to characterize ratio of inertia to friction forces (Wendt 2009)

\[ Re = \frac{\rho L u}{\eta} \]  

where \( L \) is a characteristic length. For flow in pipes this is the diameter but for flows in rectangular ducts (such as the inlet slot of the reactor) an equivalent diameter needs to be calculated (Tosun et al. 1988). For flows in pipes, flows with a Reynolds number below \( Re < 2300 \) are regarded as laminar and \( Re > 4000 \) as turbulent. In the simulation Fluent does not know which characteristic length to use and only cell Reynolds numbers are calculated based on the length scale of a mesh cell. Because a mesh cell is usually much smaller than the separation of two walls, the cell Reynolds number is much smaller than the actual Reynolds number. To get an estimate of the Reynolds number in the reactor is was calculated with the method described in Tosun et al. (1988). The inlet duct is 1x100 mm, the mixture density 0.85 kg m\(^{-3}\), the velocity 0.9 m s\(^{-1}\) and the mixture viscosity \( 1.7894 \times 10^{-5} \) kg m\(^{-1}\) s\(^{-1}\). The equivalent Reynolds number was then calculated to \( Re = 140 \). The cell Reynolds number is shown in Figure 7.12f.

\( g \) \( N_2 \) 
\( h \) Air

Figure 7.11: Thermal diffusion coefficients for each species computed by Fluent (Units: kg m\(^{-1}\) s\(^{-1}\))
7.5 Simulation results

(a) Molecular viscosity (kg m$^{-1}$ s$^{-1}$)

(b) Thermal conductivity (W m$^{-1}$ K$^{-1}$)

(c) Specific heat (J kg$^{-1}$ K$^{-1}$)

(d) Reaction rate of MBTC decomposition (Units: kmol m$^{-3}$ s$^{-1}$)

(e) Reaction rate of surface deposition (Units: kmol m$^{-3}$ s$^{-1}$)

(f) Cell Reynolds number (dimensionless)

Figure 7.12: Mixture properties, reaction rates and cell Reynolds number computed by Fluent
7.6 Comparison to experimental data

Figure 7.13 compares the deposition rate profile as predicted by FLUENT to a stationary coated sample. For better comparison the simulated profile has been mirrored along both symmetry axes. It can be seen, that both profiles have similar shapes with the highest growth rate along a central (vertical) line where unreacted gas mix from the inlet slot impinges on the substrate. On both sides of the profiles the start of the gas extraction can be seen as a defined line which separates the growth from the non-growth zone. The reduction in width of the profiles in the top and bottom region can be best explained by looking at the velocity pathlines predicted by the simulation. Figure 7.14 shows the deposition rate profile from

(a) Predicted deposition rate profile (kg m$^{-2}$ s$^{-1}$) (b) Stationary coated tin oxide sample

Figure 7.13: Qualitative comparison of simulated and experimentally found deposition profiles (not to scale)

Figure 7.13 with superimposed velocity pathlines. These lines describe the path of particles through the fluid domain from the emitting surface (inlet slot) to the outflow (extraction zone).

Due to the rectangular construction of the coating head and therewith different distances of the extraction ducts to the reaction zone, the extraction pressure is higher centrally above the substrate than on the edges. This causes flow from the edges of the substrate to be drawn towards the centre region which then results in a pointed deposition profile on two substrate edges.
As the simulation is based on an idealised design of the coating head, this effect appears to be less pronounced on the experimental sample. A possible explanation for the difference is a slightly different pressure distribution on the actual reactor compared to the model. The unsymmetrical shape of the deposited is a further indicator for an uneven pressure distribution which may be caused by structural obstacles such as holding brackets or by turbulence in the extraction pipe.

The chemical mechanism used in the simulation is known to inherit a geometry dependence which requires adjustment of the surface reaction rate in order to match experimentally observed growth rates. M. Li et al. adjusted the pre-exponential factor \( A_r \) in the Arrhenius equation of the surface deposition reaction to match their experimental value (M. Li et al. 2006). The same was done in this work. First, a glass substrate was coated stationary for 3 min. Subsequently the tin oxide film thickness was measured at the gas flow impinging point, where the highest growth rates are observed. The thickness was found to be 500 nm. With the density of tin oxide (6900 kg m\(^{-3}\)), the deposition rate was calculated in Fluent units to \(1.08 \times 10^{-5} \text{ kg m}^{-2} \text{s}^{-1}\). The pre-exponential factor was then iteratively adjusted (\( A_r = 120 \)) to give this deposition rate (see also section 7.3).
Based on this growth rate matched mechanism, the gas phase concentration of HCl predicted by the simulation and measured by the NIR diode laser has been compared. Due to the symmetry, only measurements from the slot centre to the first extraction have been considered. A common unit to describe gas phase concentrations are parts per million (ppm). To calculate this quantitatively from absorption, as measured by the laser system, the temperature in the gas phase is required. It was assumed that the temperature in gas phase is 663 K. Although it is known that the temperature profile is not uniform, this approach was chosen as a first approximation.

In case of the simulation, the ppm values can be calculated as an average from the predicted mole fractions across the substrate.

Figure 7.15 shows that the measured and predicted concentrations are qualitatively in good agreement but quantitatively lower by a factor of about five. Close to the inlet slot, where large gradients of HCl are expected, simulation and measurement differ with a more sudden rise in concentration predicted by the simulation compared to the measurement. A similar effect can be observed on the extraction side where the simulated concentration appears to drop more rapidly. Throughout the centre region of the reaction zone the concentration of HCl remains relatively constant.

The obvious quantitative difference between simulation and measurement means that the chemical mechanism used is currently not suitable to predict gas phase concentrations of HCl for quantitative comparison. One reason might be that in the actual mechanism HCl is not only created in a surface reaction but also through decomposition of MBTC in the gas phase. As long as no more detailed steps of the reaction mechanism are known, an adjustment remains difficult.
7.7 Summary

Computational fluid dynamics can be a powerful tool in the development and design of CVD coating reactors. The design of coating heads is often based on empirical studies in a time-consuming development process. CFD has the ability to simulate reactor designs prior to prototyping. Such simulations have the ability to predict flow patterns in the reactor and to optimise those in regard to precursor distribution in the reaction zone and maintaining a laminar flow field. Numerical simulations of CVD reactors rely on experimentally determined chemistry models which are usually simplifications of the real, complex, chemical reaction mechanism.

A chemical model for the deposition of tin oxide from MBTC, which is tailored to predict film growth rates, was evaluated in regard to its accuracy in quantitatively predicting chemical species distribution in the reactor gas phase. Hydrogen chloride was selected as an evaluation species and simulated concentrations of HCl were compared to previously measured concentrations (see chapter 5).

For comparison a three dimensional model based on the experimentally used APCVD reactor was built. To save computational effort, the model was reduced to one quarter of the original size.
of the actual size using the symmetry axes of the coating head. Further a steady state was assumed with a stationary substrate. The chemical model of Chae, Houf, McDaniel and Allendorf was used with identical concentrations and precursor gas flow rates as in the experiment (Chae 2006).

The deposition profile of the simulation matches the experimentally observed deposition profile well, although initially the chemical model overpredicted the growth rate near the inlet slot by several orders of magnitude. As a result the rate of the surface reaction was reduced to match the experiment (M. Li et al. 2006).

The simulation then underpredicts the observed HCl concentration by a factor of about 5, although qualitatively the concentration distribution in the coating zone appears to be predicted correctly. A possible explanation for this discrepancy is that that the reaction mechanism is oversimplified and that HCl is not only created in a surface reaction, but also in the reactor gas phase. This would lead to an overall higher concentration in HCl in the reactor. From the findings in chapter 6 and those by Chae, Houf, McDaniel and Allendorf(Chae 2006), it appears certain that MBTC is already decomposed in gas phase, which can lead to HCl formation. This is in contrast to the model where all chlorine molecules are part of the surface absorbed tin-intermediate which then reacts and forms HCl. A to this problem solution could be the postulation of a second gas phase reaction which only produces gaseous species and competes with the tin-intermediate formation. This would lower the growth rate below the inlet slot and could be set to release HCl.
8 Discussion, further work and conclusions

8.1 Discussion

8.1.1 Monitoring of APCVD process stability through in-line and in-situ spectroscopy

For the first time simultaneous monitoring of chemical species in-line and in-situ on an industrial APCVD reactor were demonstrated.

The novel in-line grating absorption spectrometer with array detector monitored the concentration of the MBTC precursor flowing into the coating head. The instrument showed good sensitivity towards variations in vapour pressure, and therewith higher precursor concentrations, of MBTC. The instrument can therefore be used to determine the bubbler fill level as well controlling the amount of precursor to the APCVD reactor. In addition the instrument can operate in multi-component gas mixtures, whereas a commercial non-optical system only functions in binary mixtures.

The in-situ diode laser absorption spectrometer monitored hydrogen chloride at multiple points in the reactor gas phase. Blockages of the coating head were simulated by altering the MBTC precursor supply to the reactor. It was demonstrated that the spectrometer instantaneously detected the resulting lower HCl concentrations. In addition, the HCl concentration distribution in the coating zone was spatially profiled. The lowest HCl concentration were found below the inlet slot due to the inflow of precursor at temperatures below the decomposition temperature. Intermittently a spike in HCl concentration was observed which was attributed to fluctuations in the flow field caused by the moving substrate.

Further in the reaction zone the instrument showed more and more stable and increasing HCl concentrations but again more fluctuations towards the extraction. It can be seen that the HCl concentration in the extraction decays and that no HCl is present in the second extraction zone. This showed that toxic gases are sufficiently contained in the coating head, which is crucial for save continuous operation of the process.
By using the monitoring results of the points in the reactor where the most stable concentration patterns were observed, a correlation to the film thickness of the deposited film was found. This means that even though HCl is a reaction by-product and not a growth initiating species, film thickness of the film can be estimated at the time of deposition through the concentration of HCl. This is an interesting aspect in quality control of tin oxide deposition. It has to be noted that to do such correlation calculations, sufficient statistical evidence has to be gathered through experimental studies. The coating system used presented large variations in thickness of the deposited films, but much smaller variations are expected in larger industrial deposition lines. For coating systems where the variation in thickness is in the order of a few nanometres, the *in-situ* monitoring will be unable to detect those variations because the NIR-LAS instrument itself has a certain signal noise level that introduced a statistical uncertainty. In addition, because the beam of the NIR-LAS instrument passed through the full length of the APCVD reactor, the HCl concentration in the extraction zone was also measured. Fluctuations in HCl concentration due to mixing with air in the extraction adds unwanted concentration fluctuations to the measurement. In larger scale reactors edge effects are less of an issue as HCl concentration is higher and the reactor much larger.

For a dual flow reactor it is concluded that only two monitoring points, one up- and one downstream of the inlet slot are sufficient to ensure safe and efficient manufacturing and to perform the aforementioned correlation calculation between optical monitoring results and film thickness.

### 8.1.2 Calculation of material savings through *in-line* and *in-situ* optical monitoring

Quality control measurements in the CVD process are performed after deposition or at the cold end of the process. During start up of the process line, a maximum time delay for a feedback of one hour can be assumed if samples have to be pulled, prepared and analysed off-line. Off-line sampling takes in this case about 40 min. If a cold end monitoring after the annealing lehr is assumed, which is the most common form of online quality control, a time delay of 20 to 30 min has to be taken into account. A hot end monitoring directly after the deposition leads to a time delay of about 5 min for a feedback on the coating process.
A float glass production line with a relatively slow line speed of 500 m h\(^{-1}\) and a substrate width of 3 m produces about 12 000 m\(^2\) of glass in a regular 8 hour shift. For common cold end process control techniques this means that about 500 to 625 m\(^2\) are produced until the process is analysed and parameters can be adjusted. A direct control of the process provides information about the coating process immediately. This leads to a process improvement of up to 5.2% per day if the start-up can be performed faster with the aid of in-line and in-situ monitoring and/or any major issue with rejects in product are avoided.

### 8.1.3 Thermal decomposition studies of the MBTC precursor

A detailed study of the decomposition of the tin oxide precursor MBTC was carried out off-line in an experiment using FTIR absorption spectroscopy. It shows the development of stable species in the decomposition of MBTC over a wide temperature range. With the addition of oxygen the decomposition of MBTC is altered compared to pure MBTC decomposition and species such as CO, CO\(_2\) and CH\(_2\)O emerge whilst CH\(_4\) appears not to be formed in the presence of oxygen.

It is known from literature that the addition of water to the MBTC-oxygen mixture accelerates the deposition rate of tin oxide significantly. The FTIR spectra of MBTC, oxygen and water are unchanged compared to those of MBTC and oxygen. This means that FTIR spectroscopy either was unable to detect the short-lived radical water is bonding with in gas phase or that water is not participating in gas phase reactions and absorbs on the substrate surface. As deposition on the walls in the experimental system can not be ruled out, it was generally difficult to establish if a stable species was created in gas phase or in the surface reaction. From the molecular structure of MBTC with the tin molecule, three bonded chlorine molecules and a carbon chain, it is however conceivable that the detected longer carbon chain molecules were a direct result of the decomposition of the C\(_4\)H\(_9\) chain from the MBTC molecule.

It was attempted to identify these decomposition molecules, although because they mainly consist of C–H bonds, these molecules share most spectral regions they appear in due to group vibrations and spectral features in the fingerprint region overlap as well. Knowing that the source of these molecules is the MBTC carbon chain, assumptions were made as to which species is likely to occur and following this these
species were tested against the recorded spectra. Spectra of species such as 1-butene, 2-butene and 1,3-butadiene were taken from a database of standard spectra which were recorded at 50°C. The spectra they were compared to are recorded in a range of 170 to 750°C where effects due to changing linestrength have a significant effect on line intensity and the peak shape. Those molecules, however, do not appear to participate in the deposition process of tin oxide.

Considering only the species driving the deposition, FTIR spectroscopy was unable to detect the tin containing intermediate. This was either due to a lack in sensitivity of the technique or due to the fact that the tin radical absorbs outside of the spectral range of the spectrometer.

Without the detection of the tin containing radical it was at this point not possible to improve the chemical mechanism used in computational simulations. It became clear, however, that the subsequently discussed chemical model largely simplifies the deposition process and species clearly identified through spectroscopy are ignored in the model reaction pathway.

8.1.4 Computational fluid dynamics modelling of an APCVD thin film deposition reactor

Based on the geometry of the experimentally used reactor, a 3D model for numerical simulation was built. The chemistry model implemented was that of Chae, Houf, McDaniel and Allendorf (Chae 2006). It was found that the experimentally observed deposition rate did not match the simulated rate. Just below the inlet the deposition rate was largely overpredicted. This has been observed previously for a different reactor system by M. Li et al. (M. Li et al. 2006). In the system used in this work the reaction rate of the surface reaction step was lowered by several orders of magnitude compared to the initial model.

The steady state simulation of the deposition profile in 3D space showed a close match to the profile observed during stationary coating of a sample substrate. After matching the growth rate to that experimentally observed, it was then of interest if the concentration of HCl would be predicted accurately by the model. It was found that qualitatively the predicted concentration profile matched that of the experiment but that qualitatively the predicted HCl concentration is lower by a factor of five. Because the chemistry model used was solely developed to predict film
growth rates and was only calibrated in respect to film thickness, it lacks complexity
that incorporates the complex gas phase reactions. Because of the qualitative match
of the adjusted model and the experiment, the simple chemistry model can still be
used in the development of new reactors and for the determination of sensor positions,
it has to noted, however, that if the geometry or the chemical composition changes
significantly the model may diverge even from the qualitative match.

8.2 Further work

In regard to further work, it is recommended to focus efforts towards detection of
the growth initiating tin intermediate. Finding this intermediate would influence
most aspects addressed in this work. The computational model could be adjusted
to provide a chemical pathway that incorporates the intermediate. This would be a
step towards a computational model that quantitatively predicts chemical species
distributions in the gas phase, which would then provide a direct link to the in-situ
optical monitoring and sensor positioning in the design stage. A step towards
finding this intermediate could be ab-initio calculations to predict vibrational spectra.
Ab-inito calculations are based on complex quantum mechanics simulations which
are approximated numerical solutions of the Schrödinger equation. This type of
numerical simulations have been used in CVD before for the estimation of activation
energies. Initial simulations (unevaluated) show that the vibrational spectra of
the SnCl₃ radical lies beyond the region of conventional FTIR operation at around
300 cm⁻¹ (Figure 8.1).

Novel external cavity quantum cascade lasers (EC-QCL) become currently more
and more available. These instruments provide a wide tuning range and are able to
operate in the mid-infrared region of light. Such EC-QCL instruments could be key
in finding the tin intermediate of MBTC but also growth initiating intermediates
of other precursors because these instruments allow monitoring in spectral regions
which are otherwise often not accessible with conventional spectroscopic techniques.

On the process monitoring side, the current laser system could be modified to a
laser absorption tomography system. In this technique multiple laser beams pass
through the coating zone simultaneously at different angles onto multiple detectors.
The grid formed through the intersection of laser beams can be mathematically
transformed into a two dimensional map. The target of this technique would be the
8.3 Conclusions

This work shows that significant material savings can be achieved on APCVD production lines through enhanced monitoring in-situ in the reactor coating zone and through in-line monitoring in the reactor feed lines. A near-infrared diode laser absorption system was used for in-situ monitoring of HCl and an infrared grating absorption spectrometer with novel pyro-electric array detector for the in-line monitoring of the precursor. The two optical instruments dedicated to these tasks provide a high sensitivity to the chemicals selected for monitoring and a rapid response to changes in process conditions.

Computational fluid dynamics modelling identified shortcomings in the flow pattern of the existing APCVD reactor system. It was demonstrated how these simulations...
can be used in the design stage to improve the design of future reactors in regard to precursor usage and uniformity of the deposited film.

The modelling work in conjunction with the spatial monitoring proofed that the APCVD reactor can operate safely without letting toxic reaction gases escape into the atmosphere.

This work can be considered as a step towards generic APCVD process understanding and control. The monitoring instruments demonstrated as well as the computational modelling can be applied in different APCVD reaction systems as well. Diode lasers can be found for a wide range of different wavelength in the near-infrared to monitor other common reaction by-products such as methane or hydrofluoric acid. Through investigations of CVD decomposition mechanisms with FTIR absorption spectroscopy stable gaseous species and possibly growth initiation radicals of other precursors can be identified. On this basis, chemical models for simulation tools such as computational fluid dynamics can be developed to provide the means for efficient reactor design and control.
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Compact grating spectrometer with a 510 element pyro-electric array detector and a integrated optical sample cell for process analysis

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This publication presents a compact grating spectrometer for the mid-infrared spectral range. A Littrow spectrograph is the core of the setup with a 510 element pyro-electric array detector. IR radiation from a SiC heating element (Globar) is guided by mirrors through a sample cell and focused on the entrance slit of the spectrograph. The spectrograph is designed with a 100 mm spherical mirror and a ruled grating with 100 lines/mm. A turning of the grating results in a variation of the spectral range which is imaged on the detector array. By using an additional mirror, the array detector can be placed orthogonal to the optical path of the spectrograph. This technical feature contributes to the compact design of the instrument. Spectra are generated by diffraction. A direct readout of the spectra with the array detector allows time resolved measurements to analyze transient processes.

The spectrometer allows the analysis of a broad mid-infrared spectral region which is well known for strong absorption bands due to the absorption of radiation by the excitation of molecule vibrations. It can be used to identify substances as well as for quantitative measurements. The instrument is equipped with a heatable optical cell positioned in front of the entrance slit of the spectrograph. An heatable sample cell expands the range of applications. Heated gases as well as evaporated infrared active substances can be analyzed. The performance of the spectrometer was evaluated by using carbon dioxide as an absorbing gas. Absorption bands of CO₂ at 2350 and 3660 cm⁻¹ were investigated which are caused by different molecule vibrations. A spectral calibration was made based on theoretical grating equations for dispersion. Measured spectra were compared to simulated spectra of the HITRAN database afterwards. Finally, spectral integrated absorbances as well as single line absorbances were measured under defined absorber conditions to evaluate quantitative measurements.

PACS numbers: Valid PACS appear here
Keywords: spectrometer, grating, pyro-thermal detector, process analysis

I. INTRODUCTION

Infrared active molecules absorb radiation because of the excitation of molecule vibrations. Many important parameters of a gas mixture, like composition, concentrations and temperature can be characterized by spectroscopic methods if spectral absorption is analyzed. Spectroscopy can be applied as an non-intrusive technique which does not interact with the medium. Low cost instruments with a compact design are essential for most applications in industrial processes. In addition, transient processes with a fast variation of conditions make real time measurements necessary and an application of spectroscopic techniques even more difficult. Instruments with single element detectors have been used for spectral resolved measurements because detectors are available for the whole mid infrared range. A spectrum can be recorded in this case based on the principle of interferometry [reference]. Scanning measurements techniques [Reference] by using rotating diffraction gratings can be applied as well. Unfortunately, moving parts in the setup limit the temporal resolution of measurement in both applications.

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The application of diffraction gratings in combination with array detectors in a spectrograph is another way to measure the spectral region of interest. In this case, the mechanical setup as well as data acquisition and processing are not as complex. Unfortunately, the availability of array detectors is very limited for the mid-infrared spectral region. Only a few types of detector arrays are suitable this spectral region. Photoconductive lead sulfide (PbS), lead selenide (PbSe) and indium antimonide (InSb) arrays belong to the group of photonic detectors. They are characterized by high detectivity and fast response time. The operating wavelength range is limited for the detector types to 1 - 3 µm (PbS), 1 - 5 µm (PbSe) and ....(InSb).

Pyro-electrical arrays belong to the group of thermal detectors. Their detectivity and response is lower compared to photonic detectors. A clear benefit of pyro-electrical detectors is the broad active spectral range. They can be applied in the whole infrared spectral range from about 1.2 to 30 µm and work without any active cooling. [references Pyreos]

Both types of line array infrared detectors were used by different groups to setup spectrographs. The spectrographs were setup using Czerny -Turner configuration which has mirrors before and after the dispersive or diffractive element. Richardson et al.¹ used a grating
spectrometer together with a 32 element InSb line array to measure carbon monoxide in the wavelength region at about 4.65 µm. Another photonic detector array (PbSe) was used by Ji et al.² for analysis. The setup was realized with CaF₂ prisms to separate a wavelength region between 1.8 - 4.9 µm. The spectrometer was applied by measuring the spectral radiation of carbon dioxide. CO₂ was emitted as a reaction product of the hydrocarbon/air combustion using a jet burner. Willing et al.³ used a 50 element pyro-electrical detector array to measure mixtures of carbon monoxide and carbon dioxide at different concentrations in the wavelength range between 4-5 µm. They investigated the absorption of CO₂ and CO mixtures.

The compact spectrometer presented in this study uses a pyro-electrical array detector as well. A 510 element array detector is integrated in a spectrograph with Littrow configuration. A 45° tilted planar mirror in the beam path of the diffracted radiation guides the radiation to the array detector which is placed orthogonal to the beam path of the spectrograph. The Littrow configuration in combination with the positioning of the detector and electronics allows a very compact spectrometer design.

The spectral region of interest in this publication is the mid-infrared wavelength range. Molecules with a dipole moment absorb radiation due to the excitation of rotation-vibration transitions. Carbon dioxide was used as an infrared active substance to test the performance of rotation–vibration transitions. Carbon dioxide was used dipole moment absorb radiation due to the excitation of the mid-infrared wavelength range. Molecules with a dipole moment absorb radiation due to the excitation of rotation-vibration transitions. Carbon dioxide was used as an infrared active substance to test the performance of rotation–vibration transitions.

II. EXPERIMENTAL SETUP

Figure 1 shows the setup of the compact infrared grating spectrometer. A 24W SiC source element is used as a miniature IR radiation source which emits radiation in a broad infrared spectral range up to 25 µm. The radiation of the light source is collected and focused on the entrance slit of the spectrograph by two parabolic gold coated mirrors. A heatable sample cell offers a path length of 55 mm. It is placed directly in front of the entrance slit of the spectrograph. The cell is equipped with KBr windows and can be heated up to 200°C.

According to the working principle of pyro-electrical detectors, a change of the radiation intensity is necessary to cause a temperature variation of the detector elements. The temperature variation influences the polarization of the detector material. This variation of the polarization can be detected as an induced voltage on the electrodes of each detector element. The temperature variation depends on the radiation energy which is characterized by the wavelength. A radiation modulation is realized by using a chopper wheel which is placed directly after the SiC element. The radiation must be modulated before it enters the heated cell to suppress avoid the detection of the infrared background radiation from the cell. An edge filter for the mid-infrared spectral range is placed in front of the sample cell to suppress visible and NIR infrared light. The spectrograph was arranged in the Littrow configuration which uses just one optical mirror. The radiation from the entrance slit is reflected by spherical mirror with a focal length of 100 mm onto a blazed diffraction grating with a line density 100 lines/mm. Depending on the tilt of the grating, a certain spectral range of diffracted radiation is reflected back into the direction of the spherical mirror. An additional 45° tilted plane mirror is positioned next to the entrance slit. It reflects the diffracted radiation with a 90° angle in the direction of the detector array. The detector and the electronic board is positioned perpendicular under the original beam path of the spectrograph. This arrangement allows a very compact design which is schematically displayed in Figure 1. A pyro-electrical line array from Pyreos Ltd (PY-LO-S-510) with 510 detector elements is used in the spectrograph. There is a pitch of 25 mm between each element which has a size of 10 µm x 867 µm. The total length of the array is 12.35 mm. A clear benefit of this type of detector is its broad spectral detectivity. The active spectral range of the detector covers the whole mid infrared radiation up to .... [reference Pyreos]. An electronic board for the array detector is provided by the manufacturer which can be used together with a PC for data acquisition. The communication is set up by a Universal Asynchronous Receiver/Transmitter (UART). Serial signals are transferred to a USB port by using a silicon labs CP2102 UART to USB bridge and virtual com port drivers on the PC. Acquisition and processing of the data was realized by using Matlab. The optical resolution depends on the setup of the spectrograph. Influencing factors are the focal length of the mirror and the groove density of the diffraction grating as well as the slit width. The spectrometer was configured by finding a trade-off between sufficient signal strength and resolution. A mirror with a short focal length was used on purpose to setup a compact instrument. Spec-
FIG. 2. Thermal crossover effects dependent on radiation modulation / Influence on signal intensities on thermal crossover effects

The slit width of ... \( \mu m \) is indicated in both figures as well. In an ideal image formation without aberrations the slit width is directly reflected and refocused on the array detector. The influence of thermal cross over effects as well as the general quality of image formation on the detector array was evaluated in our present study. Therefore, a direct image of the entrance slit on the detector array was formed by adjusting the grating orthogonal to the optical path. The grating acts like a planar mirror and radiation is directly reflected and refocused on the array detector.

The influence on image formation was analyzed by varying the modulation frequency of the radiation shown in Fig. 2 a). Radiation intensity was varied by changing the input voltage of the light source as well (see Fig. 2 b)). The slit width of ... \( \mu m \) is indicated in both figures as well. In an ideal image formation without aberrations and scattered light it should form a rectangle shape of the signal. The variation of the modulation frequency in Fig. 2 a) shows higher intensities and a broader shape of the image at lower frequencies. There is a further decrease of the signal intensity with higher frequencies. The signal broadening decreases as well but not as significant as at the beginning at lower frequencies. This test confirms the recommendation of the manufacturer to operate the sensor at frequencies higher than 10 Hz. The current spectrometer setup with its filter and radiation source is designed for the mid infrared spectral range. The low energy of infrared radiation and the limited detectivity of pyro-electrical detector allow reasonable measurements with evaluable signal intensities up to 12 Hz. An decrease of resolution has to be accepted at this point. A second test for analyzing the thermal cross over effect was performed by directly imaging the entrance slit on the array detector. The intensity of the radiation source was varied at constant modulation frequency of 27 Hz. Fig. 2 b) shows no significant influence of signal broadening by changing the intensity of radiation on the detector elements for constant modulation frequencies.

A spectral calibration was made by using the spectral dispersion

\[
\frac{d\lambda}{dx} = \frac{\cos\beta}{knf}
\]  

(1)

It characterizes the spectral range \( d\lambda \) imaged on the focal field length \( dx \) on the detector array. It is influenced by the angle \( \beta \) and the order \( k \) of diffraction as well as the line density \( n \). The linear dispersion can be multiplied with the overall length of the detector array \( 12.350 \text{ mm} \). The resulting spectral range \( d\lambda \) characterizes the part of the spectra imaged by the spectrograph on the detector array. The range is influenced by the position of the grating, the order of diffraction and the general wavelength of the absorption band. The spectral range is determined by the described method. By taking the number of detector elements in account, the spectral range per detector element can be calculated in the next step. In addition, the absolute spectral position of the measured spectra have to be determined. Measured spectra were compared to spectra given by the Hitran database. Significant spectral features like peaks or the center of the absorption band can be used to refer the measured spectra to an absolute spectral position. As a result, a linear relation between detector array elements and wavenumbers can be used for spectral calibration.

A variation of the entrance slit width was performed next to characterize the instrument performance. Fig. 3

ACKNOWLEDGMENTS

N2P project

FIG. 3. Slit variation

FIG. 4. Integrated and single line absorbance for different concentrations
Further publications in preparation

- Three dimensional computational fluids dynamics modelling of APCVD reactors validated by near-infrared absorption spectroscopy
- Compact grating spectrometer with a 510 element pyro-electric array detector for quantification of the mono-butyl-tin tri-chloride precursor
- Study of the thermal decomposition of the mono-butyl-tin tri-chloride precursor at atmospheric pressure
B FTIR spectra

The following pages present page size FTIR spectra from chapter 6.
Figure B.1: Typical FTIR spectra recorded *in-situ* in the APCVD gas phase at standard operating conditions with and without H$_2$O.
Figure B.2: Spectrum of MBTC, Bubbler temperature 100.9°C, Gas temperature in measuring cell 149.3°C, resolution 0.5 cm⁻¹.
Figure B.3: Decomposition of MBTC over a temperature range of 274 to 600°C
Figure B.4: Decomposition of MBTC at 600°C and summation of all identified decomposition species.
Figure B.5: Decomposition of MBTC with oxygen over a temperature range of 177 to 767°C
Figure B.6: Measured spectra of the thermal decomposition of MBTC and oxygen at 600°C with overlayed summation spectrum of individually identified components.
C Programming codes

The following code listings were created to run under R version 3.0.2. The plotting in code C.1 requires an installation of the R-studio code editor.

C.1 R-code for NIR-LAS post-processing

The NIR-LAS instrument records data at 10 Hz and streams each recorded spectra as a separate and numbered ASCII file into a folder. The code below can be copied into a file e.g. Processing.R. This file should reside within the folder containing the recorded spectra. It will then read each file in the correct order, fit a Lorentzian lineshape to the peak (if present) and outputs a file containing the peak area and other fitting parameters.

To visualize the fitting, the variable `plotting=TRUE` can be set in the `myf` function call. Then R-studio will display each spectra, the fitted Lorentzian lineshape and the background fitting. This is useful to adjust fitting parameters in the `lor2` function, but significantly slows down the processing. Once suitable fitting parameters are found, `plotting=` should be set to `FALSE`.

Listing C.1: Code to post-process NIR-LAS monitoring data

```r
library(minpack.lm)
library(playwith)
library(nlmrt)

#Find all data files with txt file ending
infiles ← dir(pattern='\.txt$', full.names=T)

#Define the max number of files to be read
maxfiles←length(infiles)-1

#Set up the plotting for later
#2by2 Matrix, first plot spawns two columns

#fu←
layout(matrix(c(1,1,2,3), 2, 2, byrow=TRUE),
widths = c(1,1,1,1),
height = c(1,1,1,1),
respect=F)

#layout.show(fu)

# #Whitespace around plots
par(mar=c(1,2,1,1))
```
C.1 R-code for NIR-LAS post-processing

```r
a.result <- vector()
ppmv <- vector()

#DEFINE FUNCTION THAT IS USEABLE FOR BOTH CHANNELS
myf <- function(dataset, plotting, savefile, S, Temp, L) {
  #Generating X Axis points
  xaxis <- seq(1:200)
  #Combine the axes and name variables
  dd <- cbind(xaxis, dataset) #CH1
  d <- cbind(xaxis, d$V4) #CH2
  colnames(dd) <- c('xax', 'power')
  #colnames(d) <- c('xax', 'power')
  #Convert to dataframe structure
  dd <- as.data.frame(dd)
  d <- as.data.frame(d)
  #Wavenumber conversion
  wscale <- 30/0.088
  dd$xax <- dd$xax/wscale
  d$xax <- d$xax/wscale
  #Subset the data, cut out initial ramp and peak
  xmin = 30/wscale
  peakl = 70/wscale
  peakr = 150/wscale
  dd.sub <- subset(dd, xaxis > xmin & xaxis < peakl | xaxis > peakr)
  d.sub <- subset(d, xaxis > xmin & xaxis < peakl | xaxis > peakr)
  #Do background curve fitting with ax^2 + bx + c polynomial CH1
  lmf1 <- nls(power ~ (a*xax^2) + b*xax + c, data = dd.sub, start = list(a=0.1, b=0.01, c=2), trace=F, na.action=na.exclude, algorithm='port', lower=c(0.0, 0.0), # upper=c(0.5, 2.5, 1), control = nls.control(warnOnly=T))
  #From fitted function, generate y-Axis
```
#First, generate x axis
ramp1 ← subset(dd,xax>xmin)
# ramp2 ← subset(d,xax>xamin)
x ← ramp1$xax

#Now calculate y values to x with extracted coefficients (see predict function also)
yfit1 ← (coef(lmf1)["a"]*x^2)+(coef(lmf1)["b"]*x)+(coef(lmf1)["c"])

##########################################
#CH1 LOOP
##########################################
# if (max(ramp1$power)<0.6){
# writedata1 ← cbind(0,0,0,0,0,0,0,0,0)
# write.table(writedata1, file=savefile, 
# append=T, 
# row.names=F, 
# quote=F, 
# col.names=F)
# }else{
# # Extract the peak -ln(I/I_0) log()=ln in R
peak ←− log(ramp1$power/yfit1)
# # Create data frame of x and peak values
peak.df ← as.data.frame(cbind(x,peak))
# # Find the peak center (simple method, only 1 peak)
ymax ← max(peak.df$peak)
maxi ← peak.df[peak.df$peak==ymax,]
# # Initial parameters for iteration
y0=0,
A=3.5e−4,
w=0.04,
xc=0.35
#
# # Fit Lorenzian function
# # Start list for initial values and error protection
st2←data.frame(
y0=0,
A=3.5e−4,
w=0.04,
xc=0.35
)
#
# # Levenberg-Marquart fitting algorithm
# # Fit function to data More agressive than nsl.LM
lor2←nlsb(peak ~ y0 + 2*(A/pi)*w/(4*(x-xc)^2+w^2),
control=nls.lm.control(
factor=100,
maxiter=1024,
ftol = .Machine$double.eps ,
ptol = .Machine$double.eps ),
data=peak.df ,
na.action=na.exclude,
C.1 R-code for NIR-LAS post-processing

```r
start = st2,
algorith='LM',
lower = c(-2e-4, -1e-8, 0.04, 0.3),
#upper = c(1e-6, 0.003, 0.08, 0.35),
upper = c(0.0002, 0.01, 0.07, 0.5),
trace = F)
```

```r
lory2 ← predict(lor2, data.frame(x=x))
lory2 ← lor2$coefficients["y0"] + 2 * (lor2$coefficients["A"] / pi) * lor2$coefficients["w"] / (4 * (x - lor2$coefficients["xc"])^2 + lor2$coefficients["w"]^2)
```

```r
a.result[i] ← lor2$ssquares

# Calculation of Concentration
# Line strength
# 450C → S=6.83e-21
# 500C → S=6.482e-21
# 540C → S=6.225e-21
# 600C → S=5.869e-21
P ← 1
R ← 0.0820574614 # L atm/(K mol)
Av ← 6.0221412927e23 # mol^-1
A ← lor2$coefficients[2]
atab ← 75.7587 # 75%
atab ← (1 - atab/100) + 1
ppm450C ← (A / (6.83e-21 * L)) / (P / (R * 723)) / 1000 * Av + 1e6 * atab
ppm500C ← (A / (6.482e-21 * L)) / (P / (R * 773)) / 1000 * Av + 1e6 * atab
ppm540C ← (A / (6.225e-21 * L)) / (P / (R * 813)) / 1000 * Av + 1e6 * atab
ppm600C ← (A / (5.869e-21 * L)) / (P / (R * 873)) / 1000 * Av + 1e6 * atab
```

```r
# Write certain data to file
writedata1 ← cbind(as.numeric(lor2$coefficients[2]), # A
                    as.numeric(lor2$coefficients[1]), # y0
                    as.numeric(lor2$coefficients[4]), # xc
                    as.numeric(lor2$coefficients[3]), # w
                    sigma, ppm450C, ppm500C, ppm540C, ppm600C)
```

```r
if (i==1) {
  if (file.exists(savefile) == TRUE) {
    file.remove(savefile)
  }
}```
C.1 R-code for NIR-LAS post-processing

```r
colnames(writedata1) <- c('Area', 'y0', 'xc', 'w', 'Ssquared', 'ppm450C', 'ppm500C', 'ppm540C', 'ppm600C',)
write.table(writedata1, file = savefile, row.names = F, quote = F, sep = ' ', )
else{
  write.table(writedata1, file = savefile, append = T, row.names = F, quote = F, col.names = F, sep = ' ', )
}
#
#CH1 PLOTTING
# flush.console() #force output
#
if (plotting == T){
  plot(0, type = 'n', xlim = c(0.05, 0.6), ylim = c(0, 0.02), main = 'CH1', cex = .2)
  points(x, peak, col = 'blue')
  lines(x, lory2, col = 'red')
  plot(x, ramp1$power, type = 'l', xlim = c(0.05, 0.6))
  lines(x, yfit1, col = 'red')
  points(dd.sub, col = 'green')
  abline(v = peakl)
  abline(v = peakr)
  plot(0, type = 'n', xlim = c(1, 6000), ylim = c(0, 3000))
  lines(a.result[i], col = 6, lwd = 2)
}
#Delay between each of the plots
#Important for live plotting in RStudio
Sys.sleep(0.0)
print(paste('iter', i))
print(paste('of', length(infiles)))
#}
```
**C.1 R-code for NIR-LAS post-processing**

```r
##########################################
#MAIN LOOP
##########################################
for (i in 1:maxfiles) {
  d ← read.table(infiles[i], header=F, sep=' , ')
  myf(dataset=d$V1,
       plotting=T,
       savefile=' test.dat ' ,
       #Temp = 873, #Kelvin
       # S = 5.869e-21, #cm / mol
       L = 20 # Path length in cm )
  # myf(dataset=d$V4,
  #     plotting=F,
  #     savefile='c7-Rprocessed-CH2.dat ' ,
  #     #Temp = 873, #Kelvin
  #     # S = 5.869e-21, #cm / mol
  #     L = 20 # Path length in cm )
}
##########################################
#Plotting
layout(matrix(c(1 ,1 ,1 ,1) , 1, 1, byrow=TRUE))
plot(me1$Area, type=' l ' , col=2)
# me2 ← read.table('c7-Rprocessed-CH2.dat ', header=T)
# rob1 ← read.table('CH1-processed.dat ', header=F, sep=',', flush=T)
# # # # rob2 ← read.table('c10-CH2-processed.dat ', header=F, sep=',', flush=T)
# nf ← layout(matrix(c(1,2,3,4), 1, 1, byrow=TRUE),
#     widths = c(1.1,1.2,1,1),
#     height = c(1,1,1,1),
#     respect=F)
# layout.show(nf)
# plot(rob1$V5, type=' l ', ylim=c(0, 0.0005))
# lines(me1$Ssquared , col=2)
# 'ppm450C ',
# 'ppm500C ',
# 'ppm540C ',
# 'ppm600C ')
```

---

226
C.2 R-code for FTIR post-processing

The script below reads measured FTIR spectra that reside in the folder of the script. For this the spectra should be ASCII files with a file name ending in `baselineCorr.txt` (baseline corrected spectra). The script reads a previously prepared data table named `metadata` which holds information about experimental conditions.

The script then loads standard spectra from a designated folder and calculates the absorption cross section for each spectra. Some species standard spectra are calculated by spectralcalc (Spectralcalc) because the temperature information in those spectra is more accurate than that database spectra. These are then loaded individually.

In order to subtract spectra from another, they must share identical sampling intervals on the frequency axis. The `makecompat` function fits a spline function to the standard spectra and recalculates their transmission based on the sampling intervals of the recorded spectra. The `conc` vector holds concentrations of individual species. At the end of the file extensive plotting options are given for a wide range of spectra recorded at different process temperatures.

**Listing C.2:** Code to post-process FTIR decomposition spectra of MBTC and matching to standard spectra

```r
#setwd("~/shared/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/
  baseline corrected R0.5")

# Load required Packages
library(cwhmisc)
library(playwith)
library(gtools)
library(plotrix)
```
C.2 R-code for FTIR post-processing

```r
library (caTools)
library (pracma)
#library(ggplot2)
library (reshape)
library (RColorBrewer)

# Read metadata from file. This file contains all temperature -------
#Linux
metadata ← read.table(’/home/martin/Dropbox/Work/FTIR/FTIR Monitoring/
MBTC HIGH TEMP FTIR measurements/metadata.dat’, header=TRUE)
#Windows
#metadata ← read.table(’C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/
/MBTC HIGH TEMP FTIR measurements/metadata.dat’, header=TRUE)

# Calculate a Scaling factor for all MBTC spectra -------------------------
# (below decomposition temperature)
# to make them all comparable
# Concentration C=n/V=P/(RT)
# P1=P2=P
# C1/C2=T2/T1
# So based on one reference spectra (r), all other spectra can be
# adjusted to this reference
# C = T / T_r * C_r

# LOAD a "standard" for MBTC (from Alex) ----------------------------------
MBTC.standard.conc=0.297 # mol/m3
#Mole fraction Pi/P
MBTC.standard.mf←0.01027
MBTC.standard.celltemp=149.3 # C

#Linux
MBTC.standard ← read.table (’/home/martin/Dropbox/Work/FTIR/FTIR
Monitoring/MBTC HIGH TEMP FTIR measurements/MBTC Calibration
Spectra from Alex/010_MBTC_Tgas149.3_Tbub100.9_FR0.5_1.0.txt’,
header=F)
#Windows
#MBTC.standard ← read.table(’C:/Users/Martin/Dropbox/Work/FTIR/FTIR
Monitoring/MBTC HIGH TEMP FTIR measurements/MBTC Calibration
Spectra from Alex/010_MBTC_Tgas149.3_Tbub100.9_FR0.5_1.0.txt’,
header=F)

colnames(MBTC.standard)←c(’Wavenumber’, ’Transmission’)
MBTC.standard$Wavenumber$<600 & Wavenumber<4500
MBTC.standard.abs$=−1*log(MBTC.standard$Transmission)
MBTC.standard$as.data.frame(cbind(MBTC.standard$Wavenumber,
MBTC.standard.abs))
colnames(MBTC.standard)←c(’Wavenumber’, ’Absorption’)```

ACS.path.MBTC ← MBTC.standard.abs / MBTC.standard.conc

colnames(ACS.path.MBTC) ← c('Wavenumber', 'Absorption')

ACS.path.MBTC ← as.data.frame(ACS.path.MBTC)

# Calculate Vapour pressure in bubbler
# for all datasets and add this as
# new column to the metadata

Pvapor = (10 .^ (9.1 - 1000 * 3.07 / (metadata$Tbub+273.15))) * 1.33322368 # mbar

metadata$Pvapour = Pvapor

# Mole fraction and Normalization MBTC
#Calculate the mole fraction of MBTC for all datasets

mf = metadata$Pvapour / 1013
metadata$Molefraction = mf

#Normalize the mole fraction based on one spectra
norm.mf = metadata$Molefraction / MBTC.standard.mf
metadata$norm.mf = norm.mf

#Normalize the temperature based on the temperature in the measurement cell
norm.temp = (MBTC.standard.celltemp+273.15) / (metadata$Tcell+273.15)
metadata$norm.temp = norm.temp

#Calculate a total normalization factor
# MBTC starts decomposing at around 450C so take only spectra below that
# It does not matter if they contain oxygen as it does not act on the molecule yet

# search.mbtc ← which(metadata$Toven<440)
# metadata$norm.factor ← NA
# for (i in search.mbtc){
# metadata$norm.factor[i] ← metadata$norm.mf[i] * metadata$norm.temp[i]
# }

metadata$norm.factor ← metadata$norm.mf * metadata$norm.temp

# READ IN ALL MEASURED SPECTRA
#--------------------------------------------

list ← list.files(path='.', pattern=' baselineCorr.txt$', recursive=FALSE)

for (f in list){

filename ← f

#make 'name' the filename without the 'baselineCorr' part
# e.g. 'Spectrum94' instead of 'Spectrum94-baselineCorr'
name ← substring(filename ,1 , cpos(filename , '−')-1)
number ← substring(name ,9 , nchar(name))

}
C.2 R-code for FTIR post-processing
	number ← as.numeric(number)

#Read the table
tab ← read.table(filename , header=T)

#Convert to Absorption and multiply with normalization factor
abs.spectra ← 1*log(tab$Transmission)
if(!is.na(metadata$norm.factor [number])){
  abs.spectra ← abs.spectra * metadata$norm.factor [number]
}
abs.spectra ← as.data.frame(cbind(tab$Wavenumber-0.3, abs.spectra))
colnames(abs.spectra) ← c(‘Wavenumber’, ‘Absorption’)
assign(name, abs.spectra)

# Read Standard Spectra from files---------------------------------------------------
#Linux
std.list ← list.files(path='/home/martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Standard spectra/’,
  pattern='.TXT$', recursive=FALSE, full.names=TRUE)

#Windows
#std.list ← list.files(path='C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Standard spectra/’,
#  pattern='.TXT$', recursive=FALSE, full.names=TRUE)

s.list ← c()
for(i in 1:length(std.list)){
  start ← cpos(std.list [1] , ’tra/’ ,1)+5
  stopp ← cpos(std.list [i] , ’.TXT’)-5
  strg ← substring(std.list [i] , first=start , last=stopp)
  s.list [i] ← strg
}

std.read ← lapply(std.list , read.table, header=FALSE)

for(i in 1:length(s.list)){
tmp ← std.read[[i]]
colnames(tmp) ← c(’Wavenumber’, ’Absorbance’)
#Limit the range of data to region of interest
tmp ← subset(tmp, Wavenumber ≥ 600 & Wavenumber ≤ 4500)
#Smooth data to make resolution compatible
with(tmp, runmed(Absorbance, k=9))
assign(s.list [i], tmp)
}

#std.all ← list(Allene, BiVinyl, But1Yne, Butane, Butene1, Butene2, C2H2, C2H6, C3H8, CH2O, CH4, CO2, CO, Ethene, HCl, Propene, Proplylene)
# Function to make all spectra compatible  
# =same wavenumber scale of 0.5cm⁻¹
# Required since standards are at much higher resolution

#Function that makes the x axis of imported spectra comparable to the measured spectra

## INPUTS
# file = A file that was imported such as a standard spectra or a spectracalc simulation
# basisfile= File I want to be compatible to, e.g. Measured MBTC spectra
makecompat ← function(file, basisfile){
  #Fit a spline to the imported spectra
  file.interpolate ← splinefun(file$Wavenumber, file$Absorption, method='natural')
  #Find the min and max wavenumber of the file
  min←min(file$Wavenumber)
  max←max(file$Wavenumber)
  #Extract the relevant (matching) range of the x axis from the basisfile
  compare.x←basisfile$Wavenumber[ basisfile$Wavenumber>min & basisfile$Wavenumber<max]
  #Recalculate the standard spectra with the basisfile x-range
  file.abs.interpolate←file.interpolate(compare.x)
  file.dataframe←as.data.frame(cbind(compare.x, file.abs.interpolate))
  colnames(file.dataframe)←c('Wavenumber', 'Absorption')
  basis.x←basisfile$Wavenumber
  basis.x←as.data.frame(basis.x)
  colnames(basis.x)←c('Wavenumber')
  #Now, make the spectra compatible to the complete x range of the basisfile by merging it
  rangemerge←merge(basis.x, file.dataframe, by='Wavenumber', all.x=TRUE, all.y=FALSE)
  #replace NAs with 0
  rangemerge[is.na(rangemerge)] ← 0
  #Return a dataframe that contains the standard spectra with the length of the basisfile x-axis
  return(rangemerge)
}

# Concentrations of standard species

#First create a table that holds the estimated concentrations of the species
conc←c(#0.1, #Allene
# 0.0, # CH4
# 0.1, # Butyne
# 0.015, # 1-Butene
# 0.04, # 2-Butene
# 0.08, # Butane
# 0.008, # Bivenyl


C.2 R-code for FTIR post-processing

```r
# #0.07, # Propane
# 0.04, # Ethene
# 0.05, # CO
# 0.0, # CO2
# 0.025, #CH2O
# 0.0, # HCl
# #0.2, # Isobutylen
# #0.2# Propene
#
conc ← as.data.frame(t(conc))
# colnames(conc) ← c('Allene', 'CH4', 'Butyne', 'Butene1', 'Butene2', 'Butane', 'Bivenyl', 'Propane', 'Ethene', 'CO', 'CO2', 'CH2O', 'HCl', 'Isobutylen', 'Propene')
conc ← read.table('600c_concentrations.dat', header=TRUE)
conc$CH4 ← 0.002
conc$Ethene ← 0.026
conc$Bivenyl ← 0.0015
conc$Butene2 ← 0.0032
conc$Butene1 ← 0.0045
conc$Butane ← 0.001
conc$Isobutylen ← 0.0045
conc$HCl ← 0.001
conc$Propene ← 0.001
conc$Allene ← 0.002
conc$CO2 ← 0.0015
conc$CO ← 0.001

# Loading of standard spectra
---------------------------------------------
ACS_Allene = ALLENES$Absorbance/(1.6495*10^(-6)/54.0904/0.001)
absorbance_Allene_cell = ACS_Allene * conc$Allene * 0.148
Allene.compat ← as.data.frame(cbind(ALLENES$Wavenumber, absorbance_Allene_cell))
colnames(Allene.compat) ← c('Wavenumber', 'Absorption')
Allene.compat ← makecompat(Allene.compat, basisfile=Spectrum78)

ACS_CH4 = CH4$Absorbance*log(10)/(6.605*10^(-7)/16.04/0.001)
absorbance_CH4_cell = ACS_CH4 * conc$CH4 * 0.148
CH4.compat ← as.data.frame(cbind(CH4$Wavenumber, absorbance_CH4_cell))
colnames(CH4.compat) ← c('Wavenumber', 'Absorption')
CH4_compat ← makecompat(CH4.compat, basisfile=Spectrum78)
```

232
C.2 R-code for FTIR post-processing

```r
#plot(CH2O.compat)

# 1-Butyne C4H6
# ACS_Butyne = BUT1YNE$Absorbance*log(10)/(2.4328*10^(-6)/54.0904/0.001)
# absorbance_Butyne_cell <- ACS_Butyne * conc$Butyne * 0.148
# Butyne.compat <- as.data.frame(cbind(BUT1YNE$Wavenumber,
# absorbance_Butyne_cell))
# colnames(Butyne.compat) <- c('Wavenumber', 'Absorption')
# Butyne1.compat <- makecompat(Butyne.compat ,basisfile=Spectrum78)

# 1-Butene C4H8
# ACS_Butene1 = BUTENE1$Absorbance*log(10)/(2.310*10^(-6)/56.11/0.001)
# absorbance_Butene1_cell <- ACS_Butene1 * conc$Butene1 * 0.148
# Butene1.compat <- as.data.frame(cbind(BUTENE1$Wavenumber,
# absorbance_Butene1_cell))
# colnames(Butene1.compat) <- c('Wavenumber', 'Absorption')
# Butene1.compat <- makecompat(Butene1.compat , basisfile=Spectrum78)

# 2-Butene C4H8
# ACS_Butene2 = BUTENE2$Absorbance*log(10)/(2.310*10^(-6)/56.11/0.001)
# absorbance_Butene2_cell <- ACS_Butene2 * conc$Butene2 * 0.148
# Butene2.compat <- as.data.frame(cbind(BUTENE2$Wavenumber,
# absorbance_Butene2_cell))
# colnames(Butene2.compat) <- c('Wavenumber', 'Absorption')
# Butene2.compat <- makecompat(Butene2.compat , basisfile=Spectrum78)

# Butane C4H10
# ACS_Butane = Butane$Absorbance*log(10)/(2.393*10^(-6)/58.12/0.001)
# absorbance_Butane_cell = ACS_Butane * conc$Butane * 0.148
# Butane.compat <- as.data.frame(cbind(Butane$Wavenumber,
# absorbance_Butane_cell))
# colnames(Butane.compat) <- c('Wavenumber', 'Absorption')
# Butane.compat <- makecompat(Butane.compat , basisfile=Spectrum78)

# Bivenyl / 1-3 Butadien / C4H6
# ACS_Bivenyl = BIVINYL$Absorbance*log(10)/(2.227*10^(-6)/54.0904/0.001)
# absorbance_Bivenyl_cell = ACS_Bivenyl * conc$Bivenyl * 0.148
# Bivenyl.compat <- as.data.frame(cbind(BIVINYL$Wavenumber,
# absorbance_Bivenyl_cell))
# colnames(Bivenyl.compat) <- c('Wavenumber', 'Absorption')
# Bivenyl.compat <- makecompat(Bivenyl.compat , basisfile=Spectrum78)

# Propane C3H8
# ACS_C3H8 = C3H8$Absorbance*log(10)/(1.8155*10^(-6)/44.1/0.001)
# absorbance_C3H8_cell = ACS_C3H8 * conc$Propane * 0.148
# C3H8.compat <- as.data.frame(cbind(C3H8$Wavenumber,absorbance_C3H8_cell)
# )
# colnames(C3H8.compat) <- c('Wavenumber', 'Absorption')
# Propane.compat <- makecompat(C3H8.compat , basisfile=Spectrum78)

# Ethene C2H4
```

233
C.2 R-code for FTIR post-processing

```r
# ACS_C2H4 = Ethene$Absorbance*log(10)/(1.238*10^-6)/28.05/0.001)
# absorbance_C2H4_cell = ACS_C2H4 * conc$Ethene * 0.148;
# Ethene.compat-as.data.frame(cbind(Ethene$Wavenumber,
# absorbance_C2H4_cell))
# colnames(Ethene.compat)=c('Wavenumber ','Absorption ')
# Ethene.compat=makecompat(Ethene.compat,basisfile=Spectrum78)

#Carbon Monoide CO
#Maybe better to generate from spectracalc at appropriate temperature
#ACS_CO = CO$Absorbance/((???/28.01/0.001)
#absorbance_CO_cell = ACS_CO * conc$CO * 0.148;
#CO.abs=1-CO$V2
#CO-as.data.frame(cbind(CO$V1,CO.abs))
#colnames(CO)=c('Wavenumber ','Absorption ')
#CO_compat-makecompat(file=CO,basisfile=Spectrum73)

#Carbon Dioxide CO2
#Maybe better to generate from spectracalc at appropriate temperature
# ACS_CO2 = CO2$Absorbance* log(10)/(1.812*10^-6)/44.01/0.001)
# absorbance_CO2_cell = ACS_CO2 * conc$CO2 * 0.148;
# CO2.abs=1-CO2$V2
# CO2-as.data.frame(cbind(CO2$V1,CO2.abs))
# colnames(CO2)=c('Wavenumber ','Absorption ')
# CO2_compat-makecompat(file=CO2,basisfile=Spectrum73)

#Formaldehyde CH2O
ACS_CH2O = Formaldehyde$Absorbance* log(10)/(1.2362*10^-6)/30.03/0.001)
absorbance_CH2O_cell = ACS_CH2O * conc$CH2O * 0.148;
CH2O_compat-as.data.frame(cbind(Formaldehyde$Wavenumber,
# absorbance_CH2O_cell))
 #colnames(CH2O_compat)=c('Wavenumber ','Absorption ')
#CH2O_compat-makecompat(CH2O_compat,basisfile=Spectrum78)
```

234
C.2 R-code for FTIR post-processing

#Hydrogen Chloride HCl
#Maybe better to generate from spectracalc at appropriate temperature

#Linux
HCls.read.table('/home/martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Simulated Spectra/HCL-17IC-VMR0.0062.txt', header=F)

#Windows
HCls.read.table('C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Simulated Spectra/HCL-17IC-VMR0.0062.txt', header=F)

# HCl.abs=1-HCl
HCl.as.data.frame(cbind(HCl$V1, HCl.abs))

# colnames(HCl)=c('Wavenumber','Absorption')
HCl.compat=makecompat(file=HCl, basisfile=Spectrum73)

#Isobutylene
ACS_Isobutylene = Isobutylene$Absorbance*log(10)/(3.31*10^(-6)/56.11/0.001)
absorbance_Isobutylene_cell = ACS_Isobutylene * conc$Isobutylene * 0.148;

Isobutylene.compat=as.data.frame(cbind(ACS_Isobutylene$Wavenumber, absorbance_Isobutylene_cell))

colnames(Isobutylene.compat)=c('Wavenumber','Absorption')

Isobutylene.compat=makecompat(Isobutylene.compat, basisfile=Spectrum78)

#Propene
ACS_Propene = PROPENE$Absorbance*log(10)/(1.732*10^(-6)/42.08/0.001)

absorbance_Propene_cell = ACS_Propene * conc$Propene * 0.148;

Propene.compat=as.data.frame(cbind(Propene$Wavenumber, absorbance_Propene_cell))

colnames(Propene.compat)=c('Wavenumber','Absorption')

Propene.compat=makecompat(Propene.compat, basisfile=Spectrum78)

#PLOTTING

#Colour definition for components
Measured Spectrum: red
col.spec='red'

CH4: black
col.ch4='black'

HCl
col.hcl=rgb(223,191,159, maxColorValue=255)

#1,3 Butaiene
col.13buta=rgb(255,159,64, maxColorValue=255)

#2-butene
col.2but=rgb(64,193,243, maxColorValue=255)

#1-butene
col.1but=rgb(159,64,159, maxColorValue=255)

butane
col.butane=rgb(127,191,255, maxColorValue=255)
C.2 R-code for FTIR post-processing

```r
#co2
col.co2 <- rgb(255,245,64,maxColorValue=255)

#Ethene: blue
col.ethene <- 'blue'

#CO
col.co <- rgb(255,0,217,maxColorValue=255)

#CH2O:
col.ch2o <- rgb(144,83,0,maxColorValue=255)

# PLOTTING: MBTC only thermal decomposition
#See Auswertung Alex
# playwith({
# plot(Spectrum3,type='l',ylim=c(-0.0001,0.4),xlim=c(650,4000)) #274C
# #lines(Spectrum7,col=2) #299C - identical to previous
# #lines(Spectrum13,col=3)#321C - First HCL peaks and CH4 traces
# #lines(Spectrum11,col=4)#342C -bad spectrum , bit more HCl but nothing else
# #lines(Spectrum13,col=5)#365C -still only little HCl
# #lines(Spectrum17,col=6)#352C -looks unchanged
# #lines(Spectrum19,col=7)#362C
# #lines(Spectrum21,col=8)#383C #Besides HCL and CH4 identical to Spectrum3
# #lines(Spectrum29,col=10)#382C Bit noisy, CH peak seems to change
# #lines(Spectrum49,col=10)#421C still pretty identical
# #lines(Spectrum42,col=11)#430C First Etene traces , CH peak shape changes
# #lines(Spectrum37,col=12)#426C GOOD SPECTRUM Etene clearly visible, CH peak changed
# lines(Spectrum57$Wavenumber,Spectrum57$Absorption+0.03,col=13)#470C ETENE more and more visible
# #lines(Spectrum55,col=14)#481C Noisy Spectrum, MBTC seems destroyed
# lines(Spectrum61$Wavenumber,Spectrum61$Absorption+0.06,col=15)#530C Spectrum 3-57-61 make good comparison of MBTC peak destruction
# #lines(Spectrum67,col=16)#579C No Change to previous really, more and more HCl
# lines(Spectrum78$Wavenumber,Spectrum78$Absorption+0.09,col=18)#600C GOOD Spectrum, no further decomp
# #lines(Spectrum79,col=19)#628C Noisy, identical to Spectrum 78
# })

data <- cbind(Spectrum3$Wavenumber,Spectrum3$Absorption,Spectrum57$Absorption,Spectrum61$Absorption,Spectrum78$Wavenumber,Spectrum78$Absorption)
colnames(data) <- c('Wavenumber','S3-274C','S57-470C','S61-530C','S78-Waven','S78-600C')
#head(data)
data <- as.data.frame(data)
data2 <- as.data.frame(cbind(Spectrum78$Wavenumber,Spectrum78$Absorption ))
write.table(format(data, digits=4),file='MBTC-only.dat',row.names=FALSE,quote=FALSE,sep=' ')
write.table(format(data2, digits=4),file='MBTC-onlyS78.dat',row.names=FALSE,quote=FALSE,sep=' ')
```

236
# PLOTTING: MBTC only 600C assigning components

---

# Using simulated spectra for C2H4, CO2, CH4 and HCl; PNNL spectra for the rest

# Import Simulated spectra that match Spectrum 78

# Ethene.trans ← read.table('C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Simulated Spectra/C2H4-448K-VMR0.00047.txt ')

# colnames(Ethene.trans) ← c('Wavenumber', 'Absorption')

# Ethene.compat ← makecompat(Ethene.trans, basisfile=Spectrum78)

# CO2 ← read.table('C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Simulated Spectra/CO2-448K-VMR0.000006.txt ')

# colnames(CO2) ← c('Wavenumber', 'Absorption')

# CO2.compat ← makecompat(file=CO2, basisfile=Spectrum78)

# CH4 is split into two segments, as otherwise too large for spectralcalc

# CH4.1.abs ← as.data.frame(cbind(CH4.1$V1, CH4.1.abs))

# colnames(CH4.1)<-c('Wavenumber', 'Absorption')

# CH4.1.abs ← as.data.frame(cbind(CH4.1$Wavenumber[CH4.1$Wavenumber<1100 & CH4.1$Wavenumber<1600], CH4.1.abs))

# Same for second segment

# CH4.2.abs ← as.data.frame(cbind(CH4.2$Wavenumber[CH4.2$Wavenumber<1100 & CH4.2$Wavenumber<1600], CH4.2.abs))

# Same for second segment

# CH4.1.abs ← as.data.frame(cbind(CH4.1$Wavenumber[CH4.1$Wavenumber>2700 & CH4.1$Wavenumber<3300], CH4.1.abs))

# Assign Column names and put the segments in one dataframe

# colnames(CH4.1.abs) ← c('Wavenumber', 'Absorption')

# colnames(CH4.2.abs) ← c('Wavenumber', 'Absorption')

# ch4.abs ← rbind(CH4.1.abs, CH4.2.abs)

# Merge the segments together, all other values will be 0

# ch4.merge ← merge(CH4.x, ch4.abs, by=c('Wavenumber', 'Absorption'), all=T)

# Make it compatible to the measured spectrum
C.2 R-code for FTIR post-processing

# CH4.compat ← makecompat(ch4.merge, basisfile=Spectrum78)

# # HCl
# hcl ← read.table('C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Simulated Spectra/HCl-2500-3300cm-1-448K-VNR0.00128.txt')
# hcl$V2 ← 1-hcl$
# colnames(hcl) ← c('Wavenumber','Absorption')
# hcl.merge ← merge(CH4.x,hcl,by=c('Wavenumber','Absorption'),all=T)
# HCl.compat ← makecompat(hcl, basisfile=Spectrum78)

# # Again take x axis from CO2 file, like for CH4
# colnames(hcl) ← c('Wavenumber','Absorption')
# hcl.merge ← merge(CH4.x,hcl,by=c('Wavenumber','Absorption'),all=T)
# HCl.compat ← makecompat(hcl, basisfile=Spectrum78)

# playwith(width=12,height=7,{
# plot(Spectrum78$Wavenumber,Spectrum78$Absorption,type='l')
# lines(Ethene.compat,col=2)#yes
# lines(CH4.compat,col=3)#yes
# lines(CO2.compat,col=4)#yes
# lines(Butane.compat,col=4,lwd=2)# C4H10 No clear free band
# lines(Bivenyl.compat,col=5,lwd=2)# C4H6 1,3 Butadiene no clear band
# lines(Butene2.compat,col=6,lwd=2)#C4H8 2-Butene 1450cm-1 feature
# lines(Butene1.compat,col=7,lwd=2)#C4H8 1-Butene
# lines(HCl.compat,col=8)
# #Summation of components
# lines(Spectrum78$Wavenumber,Ethene.compat$Absorption+CH4.compat$Absorption+CO2.compat$Absorption+Butane.compat$Absorption+Bivenyl.compat$Absorption+Butene1.compat$Absorption+Butene2.compat$Absorption+HCl.compat$Absorption,col=3,lty=2)
# #
# # Legend
# lg.txt ← c('Spectrum','Ethene sim','CH4 sim','CO2 sim','Butane PNNL','Bivenyl PNNL','Butene2 PNNL','Butene1 PNNL','HCl sim','Summation ')
# legend(3200,0.08,lg.txt,pch=16,lw=3,col=c(1,2,3,4,5,6,7,8,2))
# #
# arrows(1889,0.04,1889,0.005)
# text(1900,0.042,'Ethene, missing lines in simulation')
# })

# Write some datafiles for plotting in LaTeX
# data←cbind(Spectrum78,Ethene.compat$Absorption+CH4.compat$Absorption+CO2.compat$Absorption+Butane.compat$Absorption+Bivenyl.compat$Absorption+Butene1.compat$Absorption+Butene2.compat$Absorption+HCl.compat$Absorption)
# colnames(data)← c('Wavenumber','Spectrum78 ','Ethene ','Methane ','CO2 ','Butane ','Bivenyl ','Butene2 ','Butene1 ','HCl ')
# write.table(data,file='600c-decomposition-all-species.dat',quote=F,sep=' ',row.names=F,col.names=T)
# write.table(conc,file='600c-decomposition-PNNL-concentrations.dat',quote=F,sep=' ',row.names=F,col.names=T)
# summation←cbind(Spectrum78$Wavenumber,Ethene.compat$Absorption+CH4.compat$Absorption+CO2.compat$Absorption+Butane.compat$
```r
# colnames(summation) ← c('Wavenumber', 'Absorption')
# write.table(summation, file='600C-sum-spectrum.dat', quote=F, sep=' ', row.names=F, col.names=T)

# PLOTTING: MBTC + O2 thermal decomposition

# playwith(width=10, height=6, {
# plot(Spectrum2, type='l', ylim=c(-0.0001, 0.55), xlim=c(3500, 600), axes=T,
# xlab=NA, ylab=NA, xaxs = "i", yaxs = "i") #177C
# #lines(ACS.path.MBTC$Wavenumber, ACS.path.MBTC$Absorption*0.297/50, col=2)
# #lines(Spectrum8, col=2) #299C - HCl traces, CH4 traces
# #lines(Spectrum10$Wavenumber, Spectrum10$Absorption+0.03, col=3)#321C
#  - HCl and CH4 visible, CH peak change
# #lines(Spectrum12, col=4)#342C - Noisy spectrum, as previous
# #lines(Spectrum18, col=5)#352C Noisy again, otherwise no change to previous
# #lines(Spectrum20, col=6)#362C Formaldehyde traces appear
# #lines(Spectrum25, col=7)#365C Formaldehyde traces
# #lines(Spectrum22$Wavenumber, Spectrum22$Absorption+0.03, col=8)#383C
#  First CO, Formaldehyde more visible
# #lines(Spectrum31$Wavenumber, Spectrum31$Absorption+0.06, col=10)#382C
#  No CO trace, but HCl and CH4 and Formaldehyde
# #lines(Spectrum41, col=11)#433 NOISY but all species visible, lots
#  of CO
# #lines(Spectrum44$Wavenumber, Spectrum44$Absorption+0.10, col='orange')#430C GOOD spectrum, better than S41, MBTC peak still vis.S43&44
# equal good
# #lines(Spectrum58, col=13)#470C Same as previous, less and less MBTC
# #lines(Spectrum62$Wavenumber, Spectrum62$Absorption+0.14, col=14)#530C
#  Formaldehyde seems gone! LOTS CO2, ETENE
# #lines(Spectrum68, col=15)#580C Almost complete CH peak destruction. S66 already shows it
# #lines(Spectrum74$Wavenumber, Spectrum74$Absorption+0.22, col=16)#600C
#  As previous, almost complete destruction
# #lines(Spectrum80, col=18)#628C Complete destruction
# #lines(Spectrum88$Wavenumber, Spectrum88$Absorption+0.3, col=20)#767C
#  Res 1, Complete destruction
# })
# wdat ← as.data.frame(cbind(Spectrum2$Wavenumber, Spectrum2$Absorption,
# Spectrum10$Absorption, Spectrum31$Absorption, Spectrum44$Absorption,
# Spectrum62$Absorption, Spectrum74$Absorption, Spectrum88$Absorption))
# colnames(wdat) ← c('Wavenumber', '177c', '321c', '382c', '430c', '530c', '600 c', '767c')
# head(wdat)
# write.table(wdat, file='MBTC-O2-Thermal-decomposition-over-temp.dat', quote=FALSE, sep=' ', row.names=FALSE, col.names=TRUE)
```
# PLOTTING: MBTC PEAK at 1100–1200 cm⁻¹ over temperature with O₂

```r
plot(Spectrum1, type='l', ylim=c(-0.0001, 0.1), xlim=c(1000, 1350))
lines(Spectrum7, col=2)
lines(Spectrum29, col=3)
lines(Spectrum37, col=4, type='l')
lines(Spectrum57, col=5, type='l')
lines(Spectrum55, col=6, type='l')
```

# PLOTTING: 428°C spectrum MBTC+O₂: All species

```r
playwith(
  width=20,
  height=12,
  {
    colo <- c("dodgerblue2", "#E31A1C", # red
               "green4",
               "#6A3D9A", # purple
               "#FF7F00", # orange
               "black", "gold1",
               "skyblue2", "#FB9A99", # lt pink
               "palegreen2",
               "#CAB2D6", # lt purple
               "#FDBF66", # lt orange
               "gray70", "khaki2",
               "maroon", "orchid1", "deeppink1", "blue1", "steelblue4",
               "darkturquoise", "green1", "yellow4", "yellow3",
               "darkorange4", "brown")

    plot(Spectrum39$Wavenumber, Spectrum39$Absorption, col=colo[1], type='l', ylim=c(-0.001, 0.5), xlim=c(600, 4000), ylab = 'Absorption', main = 'MBTC decomposition at 428°C with added oxygen')
    lines(MBTC.standard$Wavenumber, 0.17 * MBTC.standard.abs, col=3)
    lines(Spectrum74$Wavenumber, smooth(Spectrum74$Absorption), col = colo[20])
    names <- c('Recorded spectra ', 'CO @ 171°C', 'Ethene', 'CH₄', 'CO₂ @ 171°C', 'Formaldehyde', 'Butane', 'Bivenyl', '2-Butene', '1-Butene', 'HCl')
    legend(1000, 0.45, names, col=colo, pch=20, cex=1.2, box.col = "white")
  }
)
```
C.2 R-code for FTIR post-processing

```r
# info
WithO2 ← c('yes', 'yes', 'yes', 'yes', 'yes', '?')
# info
WithoutO2 ← c('no', 'no', 'yes', 'yes', 'no', '?')
info ← as.data.frame(info)
rownames(info) ← c('CO', 'CO2', 'Ethene', 'CH4', 'Formaldehude', 'Butane ')
# addtable2plot(1000, 0.48, metadata[74,], cex=0.8, yjust=0, xpad=.2,
ypad=.5, display.rownames=TRUE, hlines)
#
# PLOTTING: 382C spectrum MBTC+O2: All species
-----------------------------
playwith(
width=20,
height=12,
{
# plot(Spectrum87, type='l', col=2)
# names←c('Spectrum', 'CO', 'Ethene', 'CH4', 'Propane', 'CH2O', 'Propene '
', 'Butene2', 'IsoButylene ')
#
# colo←rainbow(8, start=0, end=0.8)
# colo←c("dodgerblue2", "#E31A1C", red
$, "green4",
$ "#6A3D9A", purple
$ ,, "#FF7F00", orange
$ ,, "black", "gold1",
$ ,, "skyblue2", "#FB9A99", lt pink
$ ,, "palegreen2",
$ ,, "#CAB2D6", lt purple
$ ,, "#FDBF6F", lt orange
$ ,, "gray70", "khaki2",
$ ,, "maroon", "orchid1", "deeppink1", "blue1", "steelblue4",
$ ,, "darksage", "green1", "yellow4", "yellow3",
$ ,, "darkorange4", "brown")
#
# plot(Spectrum73$Wavenumber, Spectrum73$Absorption, col=colo[1], type = 'l', ylim=c(-0.001, 0.6), xlim=c(600, 4000))
# plot(Spectrum74$Wavenumber, smooth(Spectrum74$Absorption) -CO.compat$Absorption-CO2.compat$Absorption-Ethene.compat$Absorption-CH2O.compat$Absorption-Butane.compat$Absorption-Bivenyl.compat$Absorption-Butene2.compat$Absorption-Butene1.compat$Absorption-CH4.compat$Absorption-HCl.compat$Absorption
#
# plot (Spectrum22$Wavenumber, Spectrum22$Absorption
, col=colo[1], type='l', ylim=c(-0.001, 0.5), xlim=c(600, 4000), ylab = 'Absorption', main='MBTC decomposition at 342C with added oxygen')
# lines(MBTC.standard$Wavenumber, 0.17*MBTC.standard.abs, col=3)
# lines(Spectrum74$Wavenumber, smooth(Spectrum74$Absorption), col= colo[20])
# lines(CO.compat, col=colo[2])
```

C.2 R-code for FTIR post-processing

```r
# lines(Ethene.compat,col=colo[3])#yes
# lines(CH4.compat,col=colo[4])#yes
# lines(CO2.compat,col=colo[5])#yes
# lines(CH2O.compat,col=colo[6])# Formaldehyde CH2O
# lines(Butane.compat,col=colo[7],lwd=2)# C4H10
# lines(Bivenyl.compat,col=colo[8],lwd=2)# C4H6 1,3 Butadiene
# lines(Butene2.compat,col=colo[9],lwd=2)#C4H8 2-Butene
# lines(Butene1.compat,col=colo[10],lwd=2)#C4H8 2-Butene
# lines(HCl.compat,col=colo[11])
# lines(Spectrum74$Wavenumber,Butane.compat$Absorption+Bivenyl.compat$Absorption+Butene2.compat$Absorption+Butene1.compat$Absorption+CH4.compat$Absorption,col=colo[12],lwd=2)
# names=c('Recorded spectra','CO @ 171C','Ethene','CH4','CO2 @ 171C ','Formaldehyde','Butane','Bivenyl','2-Butene','1-Butene','HCl ')
# legend(1000,0.45, names,col=colo,pch=20,cex=1.2,box.col="white")
# info=c()
# info$WithO2=c('yes ','yes ','yes ','yes ','yes ','?')
# info$WithoutO2=c('no','no','yes ','yes ','no','?')
# info=data.frame(info)
# rownames(info)=c('CO','CO2 ','Ethene ','CH4 ','Formaldehyde ','Butane ')
# addtable2plot(1000,0.48,metadata[74,],cex=0.8,yjust=0,xpad=.2,
# ypad=.5,display.rownames=TRUE,hlines)
```

```r
# PLOTTING: 342C spectrum MBTC+O2: All species
---
# playwith(
# width=20,
# height=12,
# {
# #plot(Spectrum87,type='l',col=2)
# #names=c('Spectrum ','CO','Ethene ','CH4 ','Propane ','CH2O ','Propene 
# #Butene2 ','IsoButylene ')
# #colo=rainbow(8,start=0,end=0.8)
# #colo=c("dodgerblue2","#E31A1C"," red 
# "green4",
# "#6A3D9A", # purple
# "#FF7F00", # orange
# "black","gold1",
# "skyblue2","#FB9A99", # lt pink
# "palegreen2",
# "#CAB2D6", # lt purple
# "#FDBF6F", # lt orange
# "gray70", "khaki2",
# "maroon","orchid1","deeppink1","blue1","steelblue4",
# "darkturquoise","green1","yellow4","yellow3",
# "darkorange4","brown")
```
C.2 R-code for FTIR post-processing

```r
# plot(Spectrum73$Wavenumber, Spectrum73$Absorption, col=colo[1], type = 'l', ylim=c(-0.001, 0.6), xlim=c(600, 4000))
# plot(Spectrum74$Wavenumber, smooth(Spectrum74$Absorption) ~ CO.compat$Absorption - CO2.compat$Absorption - Ethene.compat$Absorption - CH20. compat$Absorption - Butane.compat$Absorption - Bivenyl.compat$Absorption - Butene2. compat$Absorption - Butene1. compat$Absorption - CH4. compat$Absorption - HCl. compat$Absorption)
# plot(Spectrum12$Wavenumber, smooth(Spectrum12$Absorption), col=colo[1], type='l', ylim=c(-0.001, 0.5), xlim=c(600, 4000), ylab='Absorption', main='MBTC decomposition at 342C with added oxygen')
# lines(MBTC.standard$Wavenumber, 0.17*MBTC.standard.abs, col=3)
# lines(Spectrum74$Wavenumber, smooth(Spectrum74$Absorption), col=colo[20])
# lines(CO.compat, col=colo[2])#yes
# lines(Ethene.compat, col=colo[3])#yes
# lines(CH4.compat, col=colo[4])#yes
# lines(CH20. compat, col=colo[5])#yes
# lines(Butane.compat, col=colo[7], lwd=2)# C4H10
# lines(Bivenyl.compat, col=colo[8], lwd=2)# C4H6 1,3 Butadiene
# lines(Butene2.comapt, col=colo[9], lwd=2)#C4H8 2-Butene
# lines(Butene1.comapt, col=colo[10], lwd=2)#C4H8 2-Butene
# lines(HCl.comapt, col=colo[11])
# lines(Spectrum74$Wavenumber, Butane.compat$Absorption + Bivenyl.comapt$Absorption +Butene2. compat$Absorption +Butene1. compat$Absorption +CH4. compat$Absorption, col=colo[12], lwd=2)
# names=c('Recorded spectra ','CO @ 171C','Ethene ','CH4 ','CO2 @ 171C','Formaldehyde CH20 '
# , 'Butane ','Bivenyl ','2-Butene ','1-Butene ','HCl ')
# legend(1000, 0.45, names, col=colo, pch=20, cex=1.2, bty="n")
# info=c()
# info$WithO2=c('yes ','yes ','yes ','yes ','yes ','yes ','yes ','yes ','yes ','yes ','yes ','yes '
# , 'yes ','yes ','yes ','yes ','yes ','yes ','yes ','yes ','yes ')
# info$WithoutO2=c('no ','no ','yes ','yes ','no ','no ','no ','no ','no ','no ','no ','no '
# , 'no ','no ','no ','no ','no ','no ','no ','no ','no ')
# info=as.data.frame(info)
# rownames(info)=c('CO ','CO2 ','Ethene ','CH4 ','Formaldehyde ','Butane ')
# addtable2plot(1000, 0.48, metadata[74,], cex=0.8, xjust=0, xpad=.2, ypad =.5, display.rownames=TRUE, hlines)
# }
# }
# # PLOTTING: 600C spectrum MBTC+O2: All species
# Recalculate some concentrations without overwriting other concentration
# vectors
conc$Butane=-0.000
conc$Butene1=-0.0027
conc$Butene2=-0.002
conc$Bivenyl=-0.003
```
C.2 R-code for FTIR post-processing

```r
# Read Ethene spectra
Ethene.trans <- read.table('C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Simulated Spectra/C2H4−448K−VMR0.00035−MBTCplusO2.txt')
colnames(Ethene.trans) <- c('Wavenumber', 'Absorption')

# Make compatibility
Ethene_compat <- makecompat(Ethene.trans, basisfile=Spectrum74)

# Read CO2 spectrum
CO2 <- read.table('C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Simulated Spectra/CO2−448K−VMR0.000103MBTCplusO2.txt')
CO2.abs <- 1 - CO2$V2
co2.compat <- as.data.frame(cbind(CO2$V1, CO2.abs))
colnames(co2.compat) <- c('Wavenumber', 'Absorption')

# Make compatibility
CO2_compat <- makecompat(file=CO2, basisfile=Spectrum74)

# # HCl
hcl <- read.table('C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Simulated Spectra/HCl−448K−VMR0.0007−MBTCplusO2.txt')
hcl$V2 <- 1 - hcl$V2
colnames(hcl) <- c('Wavenumber', 'Absorption')

# Merge HCL with CO2
hcl.merge <- merge(CO2_compat, hcl, by=c('Wavenumber', 'Absorption'), all=T)
HCl_compat <- makecompat(hcl, basisfile=Spectrum74)

# # CH4 is split into two segments, as otherwise too large for spectralcalc
CH4.1 <- read.table('C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Simulated Spectra/CH4−1100−1600cm1−448K−VMR0.0006.txt')
CH4.2 <- read.table('C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/MBTC HIGH TEMP FTIR measurements/Simulated Spectra/CH4−2700−3300cm1−448K−VMR0.0006.txt')

# Take x axis from CO2 file
CH4.x <- CO2_compat
CH4.x$Absorption <- 0

# Interpolate a spline to the segments
CH4.1.interpolate <- splinefun(CH4.1$V1, 1 - CH4.1$V2, method='natural')
CH4.2.interpolate <- splinefun(CH4.2$V1, 1 - CH4.2$V2, method='natural')

# Calculate the x,y with the correct x axis and save as data frame
CH4.1.abs <- CH4.1.interpolate(CH4.x$Wavenumber[CH4.x$Wavenumber>1100 & CH4.x$Wavenumber<1600])
```

C.2 R-code for FTIR post-processing

728 CH4.1.abs ← as.data.frame (cbind(CH4.x$Wavenumber [CH4.x$Wavenumber>1100 & CH4.x$Wavenumber<1600] , CH4.1.abs))
729 #Same for second segment
730 CH4.2.abs ← CH4.2.interpolate (CH4.x$Wavenumber [CH4.x$Wavenumber>2700 & CH4.x$Wavenumber<3300])
731 CH4.2.abs ← as.data.frame (cbind(CH4.x$Wavenumber [CH4.x$Wavenumber>2700 & CH4.x$Wavenumber<3300] , CH4.2.abs))
732 #Assign Column names and put the segments in one dataframe
733 colnames(CH4.1.abs) ← c('Wavenumber' , 'Absorption ')
734 colnames(CH4.2.abs) ← c('Wavenumber' , 'Absorption ')
735 ch4.abs ← rbind(CH4.1.abs , CH4.2.abs)
736 #Merge the segments together, all other values will be 0
737 ch4.merge ← merge(CH4.x, ch4.abs , by=c('Wavenumber' , 'Absorption '), all=T)
738 #Make it compatible to the measured spectrum
739 CH4.compat ← makecompat(ch4.merge , basisfile=Spectrum74)

740 #Formaldehyde
741 ch2o.sim ← read.table ( 'C:/Users/Martin/Dropbox/Work/FTIR/FTIR Monitoring/ MBIC HIGH TEMP FTIR measurements/Simulated Spectra/ CH2O−448K−VMR0.00021.txt')
742 head(ch2o.sim)
743 ch2o.sim$V2 ← 1−ch2o.sim$V2
744 colnames(ch2o.sim) ← c('Wavenumber' , 'Absorption ')
745 CH2O.compat ← makecompat(ch2o.sim , basisfile=Spectrum74)

746 #1-Butene C4H8
747 absorbance_Butene1_cell ← ACS_Butene1 * conc$Butene1 * 0.148
748 Butene1.compat ← as.data.frame (cbind(BUTENE1$Wavenumber, absorbance_Butene1_cell))
749 colnames(Butene1.compat) ← c('Wavenumber' , 'Absorption ')
750 Butene1.compat ← makecompat(Butene1.compat , basisfile=Spectrum74)

751 #2-Butene C4H8
752 absorbance_Butene2_cell ← ACS_Butene2 * conc$Butene2 * 0.148
753 Butene2.compat ← as.data.frame (cbind(BUTENE2$Wavenumber, absorbance_Butene2_cell))
754 colnames(Butene2.compat) ← c('Wavenumber' , 'Absorption ')
755 Butene2.compat ← makecompat(Butene2.compat , basisfile=Spectrum74)

756 #Butane C4H10
757 absorbance_Butane_cell = ACS_Butane * conc$Butane * 0.148
758 Butane.compat ← as.data.frame (cbind(Butane$Wavenumber, absorbance_Butane_cell))
759 colnames(Butane.compat) ← c('Wavenumber' , 'Absorption ')
760 Butane.compat ← makecompat(Butane.compat , basisfile=Spectrum74)

761 #Bivenyl /1-3 Butadien /C4H6
762 ACS_Bivenyl = BIVINYL$Absorbance * log(10)/(2.227*10^−6−6)/54.0904/0.001
763 absorbance_Bivenyl_cell = ACS_Bivenyl * conc$Bivenyl * 0.148
764 Bivenyl.compat ← as.data.frame (cbind(BIVINYL$Wavenumber, absorbance_Bivenyl_cell))
765 colnames(Bivenyl.compat) ← c('Wavenumber' , 'Absorption ')
766 Bivenyl_compat ← makecompat(Bivenyl.compat , basisfile=Spectrum74)
C.2 R-code for FTIR post-processing

```r
playwith(width=12,
height=8,
{
plot(Spectrum74,type='l',col=col.spec,ylim=c(-0.001,0.13),xlim=c(3500,600),axes=T,xlab=NA,ylab=NA,xaxs = "i",yaxs = "i")
# lines(CO.compat$Wavenumber,CO.compat$Absorption,col=col.co)#yes
# lines(Ethene.compat,col=col.ethene)#yes
# lines(CH4.compat,col=col.ch4)#yes
# lines(CO2.compat,col=col.co2)#yes
# lines(CH2O.compat$Wavenumber,CH2O.compat$Absorption,col=col.ch2o)#
# Formaldehyde CH2O
#lines(HCl.compat,col=col.hcl)
#lines(Butane.compat,col=col.butane,lwd=2,lty=2)# C4H10
# lines(Bivenyl.compat,col=col.13buta,lwd=2)# C4H6 1,3 Butadiene
# lines(Butene2.compat,col=col.2but,lwd=2)#C4H8 2-Butene
# lines(Butene1.compat,col=col.1but,lwd=2)#C4H8 1-Butene

lines(Spectrum74$Wavenumber,
Butane.compat$Absorption+
Bivenyl.compat$Absorption+
Butene2_compat$Absorption+
Butene1_compat$Absorption+
CH2O.compat$Absorption+
HCL.compat$Absorption+
Ethene.compat$Absorption+
CO.compat$Absorption+
CO2.compat$Absorption+
CH4.compat$Absorption,
col="black",lwd=2,lty=2)
# lines(Spectrum74$Wavenumber,Spectrum74$Absorption-(Butane_compat$Absorption+  
# Bivenyl.compat$Absorption+  
# Butene2_compat$Absorption+  
# Butene1_compat$Absorption+  
# CH2O_compat$Absorption+  
# HCL.compat$Absorption+  
# Ethene.compat$Absorption+  
# CO_compat$Absorption+
# CO2_compat$Absorption+  
# CH4_compat$Absorption),
# col44,lwd=2,lty=3)
# names<-c('Recorded spectra','CO @ 171C','Ethene','CH4','CO2 @ 171C','Formaldehyde','HCl','Butane','Bivenyl','2-Butene','1-Butene')
# legend(1500,0.035, names=col=c(col.spec,col.co,col.ethene,col.ch4,col.co2,col.ch2o,col.hcl,col.butane,col.13buta,col.2but,col.1but),pch=20,cex=1.2,box.col = "white")

#info<-c()
#info$WithO2<-c('yes','yes','yes','yes','yes','?')
#info$WithoutO2<-c('no','no','yes','yes','no','?')
```
C.2 R-code for FTIR post-processing

```r
#info ← as.data.frame(info)
rownames(info) ← c('CO','CO2 ','Ethene ','CH4 ','Formaldehyde ','Butane ')
addtable2plot (1000,0.48,metadata[74,],cez=0.8,yjust=0,xdad=.2,ypad=.5,display.rownames=TRUE,hlines)
abline(h=0.13,lwd=0.01)
abline(h=-0.001)
}
#
#
# PLOTTING: 600C 2500-3200 wavenumber range
------------------
playwith(
  width=20,
  height=12,
  {
    plot(Spectrum87,type='l',col=2)
    names=c('Spectrum ','CO','Ethene ','CH4 ','Propane ','CH2O ','Propene ','Butene2 ','IscButylene ')
    colo ← rainbow(8,start=0,end=0.8)
    colo ← c("dodgerblue2","#E31A1C", # red
    "green4",
    "#6A3D9A", # purple
    "#F7F7F0", # orange
    "black","gold1",
    "skyblue2","#FB9A99", # lt pink
    "palegreen2",
    "#CAB2D6", # lt purple
    "#FDBF6E", # lt orange
    "gray70", "khaki2",
    "maroon","orchid1","deeppink1","blue1","steelblue4",
    "darkturquoise","green1","yellow4","yellow3",
    "darkorange4","brown")
    plot(Spectrum73$Wavenumber,Spectrum73$Absorption,col=colo[1],type='l',ylim=c(-0.001,0.6),xlim=c(600,4000))
    plot(Spectrum74$Wavenumber,smooth(Spectrum74$Absorption)-CO.compat$Absorption-CO2.compat$Absorption-Ethene.compat$Absorption-CH2O.compat$Absorption-Butane.compat$Absorption-Bivenyl.compat$Absorption-Butene2.compat$Absorption-Butene1.compat$Absorption-Ch4.compat$Absorption-HCl.compat$Absorption
    plot(Spectrum74$Wavenumber,smooth(Spectrum74$Absorption)
      ,col=colo[1],type='l',ylim=c(-0.001,0.2),xlim=c(2500,3200),
ylab='Absorption',main='MBTC decomposition at 600C with added oxygen ')
    lines(MBTC.standard$Wavenumber, Spectrum2$Absorption-0.135*MBTC.standard.abs,col=3)
```

C. 2 R-code for FTIR post-processing

```r
# lines(Spectrum74$Wavenumber, smooth(Spectrum74$Absorption), col= colo[20])
# lines(CO.comapt, col=colo[2])#yes
# lines(Ethene.comapt, col=colo[3])#yes
# lines(CH4.comapt, col=colo[4])#yes
# lines(CO2.comapt, col=colo[5])#yes
# lines(CH2O.comapt, col=colo[6])# Formaldehyde CH2O
# lines(Butane.comapt, col=colo[7], lwd=2)# C4H10
# lines(Bivenyl.comapt, col=colo[8], lwd=2)# C4H6 1,3 Butadiene
# lines(Butene2.comapt, col=colo[9], lwd=2)# C4H8 2-Butene
# lines(Butene1.comapt, col=colo[10], lwd=2)# C4H8 2-Butene
# lines(HCl.comapt, col=colo[11])
# lines(Spectrum74$Wavenumber, Butane.comapt$Absorption + Bivenyl.comapt$Absorption + Butene2.comapt$Absorption + Butene1.comapt$Absorption + CO2.comapt$Absorption, col=colo[12], lwd=2)
# names=c('Recorded spectra', 'CO @ 171C', 'Ethene', 'CH4', 'CO2 @ 171C', 'Formaldehyde', 'Butane', 'Bivenyl', '2-Butene', '1-Butene', 'HCl')
# legend(2500, 0.2, names, col=colo, pch=20, cex=1.2, box.col = "white")
```

```
```
C.2 R-code for FTIR post-processing

```r
# "darkturquoise","green1","yellow4","yellow3",
# "darkorange4","brown")

# plot(Spectrum73$Wavenumber, Spectrum73$Absorption, col=colo[1], type ="l", ylim=c(-0.001,0.6), xlim=c(600,4000))
# plot(Spectrum74$Wavenumber, smooth(Spectrum74$Absorption)
# -CO.compat$Absorption-CO2.compat$Absorption-Butane.compat$Absorption-Bivenyl.compat$Absorption-Butene2.compat$Absorption-Butene1.compat$Absorption-CH4.compat$
# Absorption-HCl.compat$Absorption

# plot(Spectrum74$Wavenumber, smooth(Spectrum74$Absorption)
# ,col=colo[1], type='l', ylim=c(-0.001,0.2), xlim=c(600,1900), ylab='Absorption ', main='MBTC decomposition at 600C with added oxygen ')
# lines(MBTC.standard$Wavenumber, Spectrum2$Absorption-0.135*MBTC.standard.abs, col=3)
# lines(Spectrum74$Wavenumber, smooth(Spectrum74$Absorption), col=colo[20])
# lines(CO.compat, col=colo[2])#yes
# lines(Ethene.compat, col=colo[3])#yes
# lines(CH4.compat, col=colo[4])#yes
# lines(CO2.compat, col=colo[5])#yes
# lines(CH2O.compat, col=colo[6])# Formaldehyde CH20
# lines(Butane.compat, col=colo[7], lwd=2)# C4H10
# lines(Bivenyl.compat, col=colo[8], lwd=2)# C4H6 1,3 Butadiene
# lines(Butene2.compat, col=colo[9], lwd=2)#C4H8 2-Butene
# lines(Butene1.compat, col=colo[10], lwd=2)#C4H8 2-Butene
# lines(HCl.compat, col=colo[11])
# lines(Spectrum74$Wavenumber,Butane.compat$Absorption+
# Bivenyl.compat$Absorption+Butene2.compat$Absorption+Butene1.compat$Absorption+CH4.compat$Absorption, col=colo[12], lwd=2)
# names=c('Recorded spectra ','CO @ 171C','Ethene ','CH4 ','CO2 @ 171C ','Formaldehyde ','Butane ','Bivenyl ','2-Butene ','1-Butene ','HCl ')
# legend(6000,0.2, names, col=colo, pch=20, cex=1.2, box.col = "white")
# info=c()
# info$WithO2=c('yes ','yes ','yes ','yes ','yes ','no','?')
# info$WithoutO2=c('no ', 'no ', 'yes ', 'yes ', 'no ', 'no ', '?')
# info<-as.data.frame(info)
# rownames(info)<-c('CO','CO2 ','Ethene ','CH4 ','Formaldehude ','Butane ')
# # addtable2plot (1000, 0.48, metadata[74,], cex=0.8, yjust=0, xpad=.2, ypad=.5, display.rownames=TRUE, hlines)
# }

# PLOTTING: 600C Summation of individual components

------------------------
```

```r
# playwith(
# width=12,
# height=8,
#
# # plot(Spectrum87, type='l', col=2)
```
# names <- c('Spectrum', 'CO', 'Ethene', 'CH4', 'Propane', 'CH2O', 'Propene', 'Butene2', 'IsoButylene')
#
# colo <- rainbow(8, start=0, end=0.8)
#
# colo <- c("dodgerblue2", "#E31A1C", "red",
# "#6A3D9A", "purple",
# "#FF7F00", "orange",
# "black", "gold1",
# "skyblue2", "#FB9A99", "lt pink",
# "palegreen2",
# "#CAB2D6", "lt purple",
# "#FDBF6E", "lt orange",
# "gray70", "khaki2",
# "maroon", "orchid1", "deepink1", "blue1", "steelblue4",
# "darkturquoise", "green1", "yellow4", "yellow3",
# "darkorange4", "brown")

plot(Spectrum74$Wavenumber, smooth(Spectrum74$Absorption)
, col=colo[1], type='l', ylim=c(-0.001, 0.5), xlab=c(600, 4000), ylab = 'Absorption', main='MBTC decomposition at 600C with added oxygen')

lines(Spectrum74$Wavenumber, CO.compat$Absorption+Ethene.compat$Absorption+CH4.compat$Absorption+CO2.compat$Absorption+CH2O.compat$Absorption+Butene1.compat$Absorption+Butene2.compat$Absorption+HCl.compat$Absorption, col=colo[2])

# names <- c('Recorded spectra', 'All components')

legend(1000, 0.45, names, col=colo, pch=20, cex=1.2, box.col = "white")

#

# PLOTTING: 600C difference between with and without O2 and H2O

---

playwith(width=20, height=12, {
  # plot(Spectrum87, type='l', col=2)
  # names <- c('Spectrum', 'CO', 'Ethene', 'CH4', 'Propane', 'CH2O', 'Propene', 'Butene2', 'IsoButylene')
  #
  # colo = rainbow(8, start=0, end=0.8)
  #
  # colo = c("dodgerblue2", "#E31A1C", "red",
  # "#6A3D9A", "purple",
  # "#FF7F00", "orange",
  # "black", "gold1",
  # "skyblue2", "#FB9A99", "lt pink",
  # "palegreen2",
  # "#CAB2D6", "lt purple",
  # "#FDBF6E", "lt orange"
}
C.2 R-code for FTIR post-processing

```r
# "gray70", "khaki2",
# "maroon", "orchid1", "deeppink1", "blue1", "steelblue4",
# "darkturquoise", "green1", "yellow4", "yellow3",
# "darkorange4", "brown")
#
# plot(Spectrum74$Wavenumber,smooth(Spectrum74$Absorption)
# ,col=colo[1],type='l',ylim=c(-0.001,0.5),xlim=c(600,4000),ylab = 'Absorption ',main='MBTC decomposition at 600C with and without oxygen')
# lines(Spectrum73$Wavenumber,smooth(Spectrum73$Absorption),col=colo [2])
# lines(Spectrum75$Wavenumber,smooth(Spectrum75$Absorption),col=colo [3])
# names=c('With oxygen ','Without oxygen ','With oxygen and water ')
# legend(1000,0.45 ,names ,col=colo ,pch=20,cex=1.2,box.col = "white")
# })
#
# Search in Metadata
------------------------------------------------------
# search←which(metadata$Resolution==0.5 &
# metadata$Toven<400 &
# metadata$OxygenFlow==30 &
# metadata$Tbub≥70 )
#
#alternatively , just provide a vector of spectra numbers
#numbers are the row numbers in metadata
#metadata
#search←c(93)
#
#save the metadata of this search
#plotmetadata←metadata[search ,]
#
#select the spectra that match the search criteria
#search←list[search]
#
#Generate empty vector that later stores the spectra name. will be used in
#plot-legend
#names←c()
#
#Define a colour for each spectrum, will be used in loop and legend while plotting
#colours←rainbow(length(metadata),start=0,end=max(1,length(metadata)-1)
#/length(metadata))
#
# PLOTTING: Loop for plotting spectra matching search
---------------------
playwith({
# # #Create an empty plot, this makes it easy to add lines ni the loop
# plot(1, type="n", xlim=c(600,4500),ylim=c(0,0.3))
#
# for (i in 1:length(search)){
```
C.2 R-code for FTIR post-processing

```r
# Make the 'filename' item i from the list
filename <- search[i]
# name the 'baselineCorr' part
# e.g. 'Spectrum94' instead of 'Spectrum94-baselineCorr'
name <- substring(filename, 1, cpos(filename, '-') - 1)
# Read the table
tab <- read.table(filename, header=T)
# Convert to Absorption
abs.spectra <- -1 * log(tab$Transmission)
abs.spectra <- as.data.frame(cbind(tab$Wavenumber, abs.spectra))
colnames(abs.spectra) <- c('Wavenumber', 'Transmission')
# Assign this name a spectrum (read from table) and save it temporarily
# head(tab)
# tmp <- assign(name, tab)
# head(tmp)
# Just for plotting, plot the spectrum and change colour
# lines(abs.spectra$Wavenumber - 0.45, abs.spectra$Transmission, col = colours[i])
# Sys.sleep(0.0)
# names[i] <- name
# TESTING ONLY
# lines(HCl$Wavenumber, HCl$Transmission * 300, col = 3)
# }
# names <- names[!is.na(names)]
# legendaddition <- cbind(names, plotmetadata)
# legend(600, 0.25, names, col = colours, pch = 20, cex = 0.8)
# Adds the metadata table to the plot
# addtable2plot(1200, 0.25, legendaddition, cex = 0.8, yjust = 0)
# }
```

252