Real-time optical characterization of ammonia (NH₃) by UV absorption spectroscopy

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http://www.phy-astr.gsu.edu/dietzrg/HPCVD.html

Last update: Jan. 10, 2005
Advantage of UV spectroscopy to study precursor decomposition dynamics

- optical detection below 400 nm eliminates interference with radiation from heated substrate/gas phase:
  - UV absorption
  - Luminescence
  - Raman spectroscopy
  - Light Scattering
Ammonia (NH$_3$) Characterization

- $NH_3$ UV-transmission spectra
- Continuous $NH_3$ flow: Sensitivity
- Decomposition of $NH_3$
- Pulsed $NH_3$ flow
Characterization of NH$_3$ UV-absorption

Reactor pressure: 1630 mbar
NH$_3$ flow: 1000 sccm = 100% FS
diluted in N$_2$-Main flow: 5 slm

NH$_3$ absorption

transmitted intensity (a.u.)

wavelength (nm)
Characterization of NH$_3$ UV-absorption: MFC-I

Reactor pressure: 1630 mbar
NH$_3$ flow diluted in N$_2$ - Main flow: 5 slm

100%FS = 1000 sccm
Characterization of NH₃ UV-absorption: MFC-II

NH₃ absorption
100%FS = 2 sccm

Reactor Conditions:
Pressure: 1630 mbar
Temperature: 23 °C
N₂ Main Flow: 5 slm
NH₃ characterization: Absorption maxima

The total flow of gases through the HPCVD reactor is given by

\[ F = F_{\text{Main}_N} + F_{\text{NH}_3} = 0.5 \cdot z + 1 \cdot 10^{-2} \cdot y \text{ [slm]} \]

The molar ammonia flow ratio \( \chi \) through the reactor is given by

\[ \chi = \frac{n_{\text{NH}_3}}{n_{\text{total}}} = \frac{n_{\text{NH}_3}}{n_{\text{Main}_N} + n_{\text{NH}_3}} = \frac{y}{50 \cdot z + y} \]

where \( z \) and \( y \) are the percentage of flow full scale (FS) with 50 slm and 1 slm, respectively.

Absorption maxima vs. NH₃ flow ratio \( \chi \)

NH₃ flow ratio \( \chi \) (10⁻²)

Absorption peak-maxima (10⁻² cm⁻¹)

NH₃ absorption @ 217.105 nm
Steady-state NH₃ flow condition
Reactor pressure: 1600 mbar
\( N_2 \)-Main flow: 5 slm

\[ \alpha(\chi)_{\text{peak}} = 0.38 \cdot \ln(\chi + 0.011) - 2.0 \cdot \chi + 1.73 \text{ [cm}^{-1}] \]

Absorption maxima vs. NH₃ flow ratio \( \chi \)

NH₃ flow ratio \( \chi \) (10⁻²)

Absorption peak-maxima (10⁻² cm⁻¹)

NH₃ absorption @ 221.6 nm
Steady-state NH₃ flow condition
Reactor pressure: 1600 mbar
\( N_2 \)-Main flow: 5 slm

\[ \alpha(\chi)_{\text{peak}} = [ - 45.0 + 45.01 \cdot \exp(\chi / 18) ] \cdot 10^{-2} \text{ [cm}^{-1}] \]
The number concentration of NH$_3$ molecules per time unit as a function of the observed absorption at

$\lambda = 221.6$ nm

\[ N_{NH_3(\lambda=221.6\text{nm})} = \frac{7.17 \cdot 10^{21} \cdot z \cdot \ln \alpha'}{1 - 32 \cdot \ln \alpha'} \quad [\text{s}^{-1}] \]

with \( \alpha' = \frac{\alpha_{221.6\text{nm}}}{80.01} - 80 \)

Absorption line at $\lambda = 221.6$ nm sensitive for NH$_3$ concentrations in the range: $10^{+19} - 10^{+21}$
Absorption peak maxima correlate linearly with $NH_3$ flow ratio $\chi$ in a double log scale.

**Sensitivity to $NH_3$ concentrations**

- $\lambda = 224.8$ nm \((10^{21} - 10^{24})\)
- $\lambda = 221.6$ nm \((10^{18} - 10^{21})\)
- $\lambda = 217.1$ nm \((10^{17} - 10^{19})\)
- $\lambda = 213.07$ nm \((10^{16} - 10^{18})\)
- $\lambda = 209.21$ nm \((10^{15} - 10^{17})\)
- $\lambda = 205.38$ nm \((10^{14} - 10^{17})\)
- $\lambda = 201.81$ nm \((? - 10^{16})\)
- $\lambda = 198.14$ nm \((? - 10^{16})\)
- $\lambda = 194.62$ nm \((? - 10^{15})\)
Decomposition of NH$_3$

**NH$_3$ decomposition**

- **NH$_3$ = 20 sccm diluted in 5slm N$_2$ main flow**

**NH$_3$ decomposition**

- **RT**
- **690K**
- **800K**
- **900K**
- **990K**
- **1070K**
- **1140K**
- **1200K**

**Absorption peak-amplitude (cm$^{-1}$)**

- **20 sccm NH$_3$ diluted in 5 slm N$_2$ carrier gas**

**Temperature [K]**

- **205.4 nm**
- **209.2 nm**
- **213 nm**
- **217.1 nm**
- **221.6 nm**
- **224.8 nm**

**Energy (eV)**

- 6.20
- 5.90
- 5.64
- 5.39

**Absorption (cm$^{-1}$)**

- 0.8
- 0.6
- 0.4
- 0.2
- 0.1

**Wavelength (nm)**

- 200
- 210
- 220
- 230

**RT**

**690K**

**800K**

**900K**

**990K**

**1070K**

**1140K**

**1200K**
NH₃ flow characterization: Pulsed Injection

Transmission traces monitored at $\lambda = 221.6\ nm$ during NH₃ precursor pulse injection in the reactor at 1.6 bar and a total flow through the reactor of 5slm. The NH₃ flow was varied from 10 – 500 sccm (1 - 50%FS). The cycle sequence is 6 s with a 1 s NH₃ pulse width.
NH₃ flow characterization: Pulsed Injection

Absorption traces monitored at

\( \lambda = 221.6 \text{ nm} \)

Reactor main flow:

5slm

NH₃ flow through the reservoir:

200 sccm

Reactor pressure:

1bar - 12.5 bar

Distinct features:

- a systematic shift in the pulse arrival time,
- a systematic NH₃ pulse broadening,
- a change in NH₃ absorption cross section for \( p > 8 \text{ bar} \).
NH$_3$ flow characterization: Pulsed Injection

Main flow increased to 10 slm!  NH$_3$ pulses sharpened
NH₃ flow characterization: Pulsed Injection

Precursor pulse delay / broadening as function of flow rate at constant reactor pressure

Monitoring:
\[ \lambda = 221.6 \text{ nm} \]

Cycle repetition rate:
6 sec

NH₃ pulse width:
1 sec

NH₃ flow:
20%FS = 200 sccm

Reactor pressure:
p = 10 bar


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