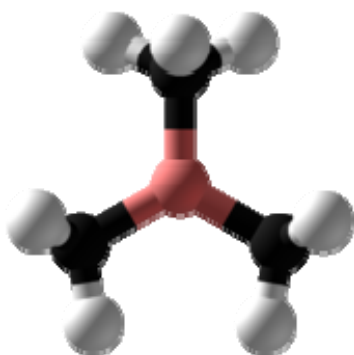# A surface inhibiting effect in chemical vapor deposition of boron-carbon thin films from trimethylboron

Laurent Souqui, Hans Högberg, Henrik Pedersen
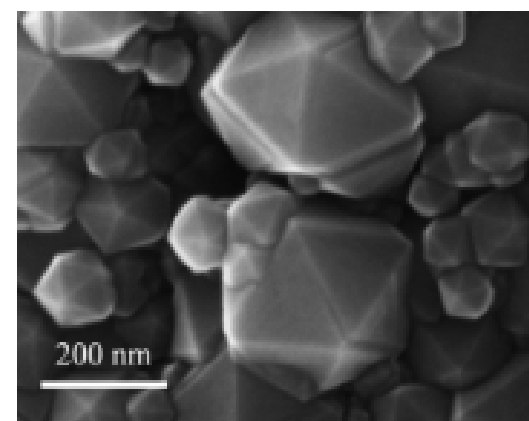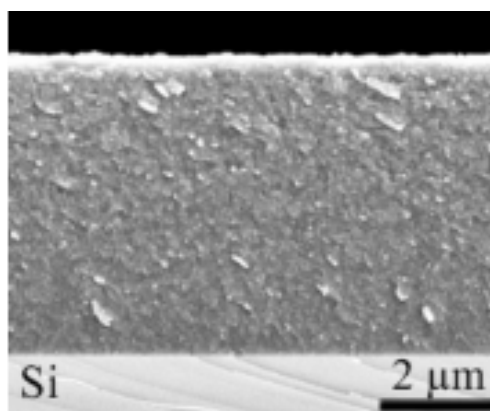
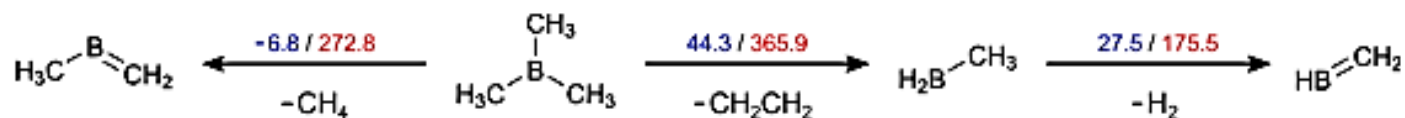*Department of Physics, Chemistry and Biology*

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# Boron-Carbon films from Trimethylboron



- Very few studies
- Investigated gas phase chemistry:
  - Between 500 °C and 1200 °C
  - Pyrolysis starts around 650 °C
  - Amorphous and crystalline boron carbide

## Trimethylboron
## $B(CH_3)_3$
## TMB



Imam, M.; Souqui, L.; Herritsch, J.; Stegmüller, A.; Höglund, C.; Schmidt, S.; Hall-Wilton, R.; Högberg, H.; Birch, J.; Tonner, R.; Pedersen, H. Gas Phase Chemistry of Trimethylboron in Thermal Chemical Vapor Deposition. *J. Phys. Chem. C* **2017**, *121*, 26465–26471.
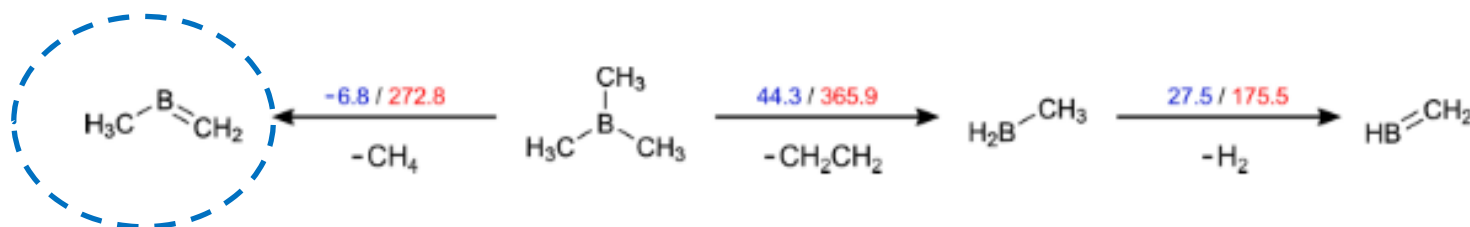
# Boron-Carbon films from Trimethylboron

## From Quantum chemical calculations:
## Decomposition in Ar ambient at 800 °C



Imam, M.; Souqui, L.; Herritsch, J.; Stegmüller, A.; Höglund, C.; Schmidt, S.; Hall-Wilton, R.; Högberg, H.; Birch, J.; Tonner, R.; Pedersen, H. Gas Phase Chemistry of Trimethylboron in Thermal Chemical Vapor Deposition. *J. Phys. Chem. C* **2017**, *121*, 26465−26471.
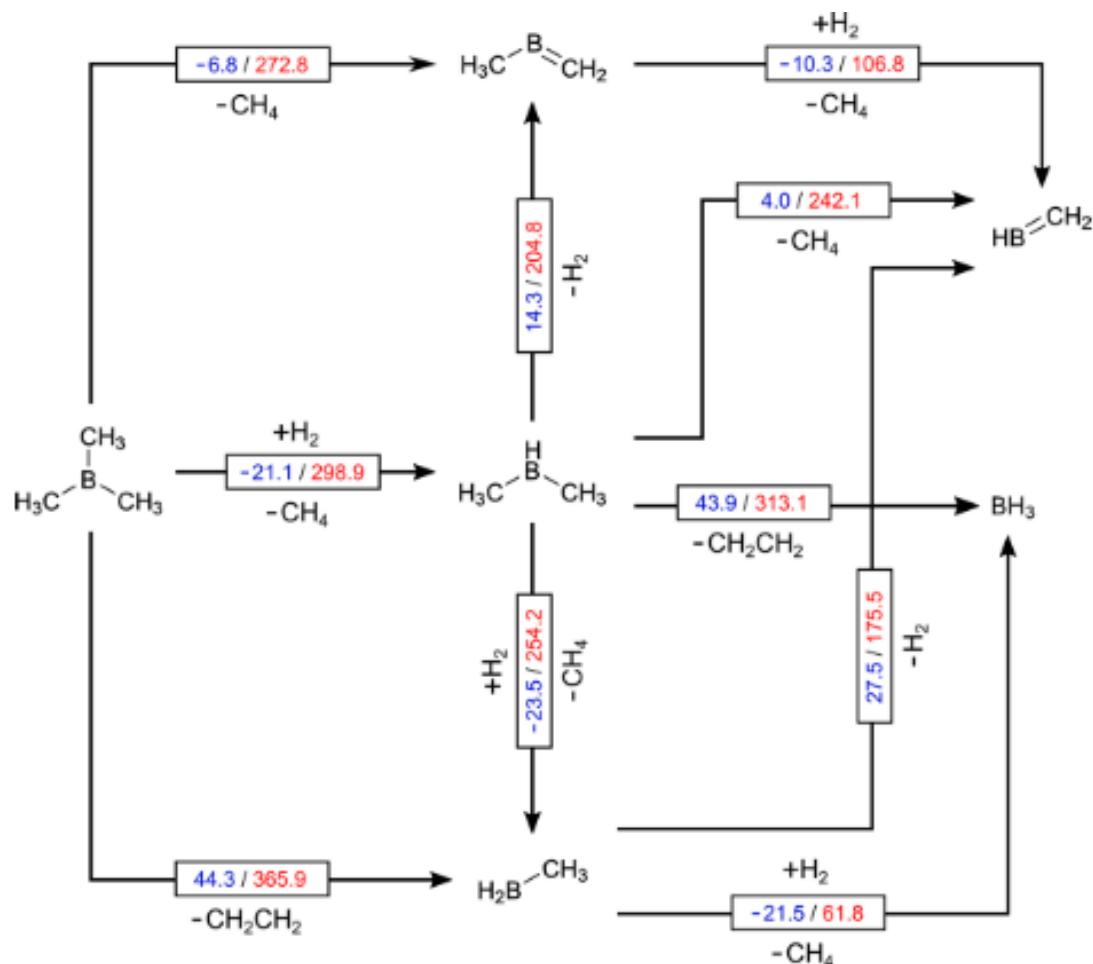
# Boron-Carbon films from Trimethylboron

From Quantum chemical calculations:
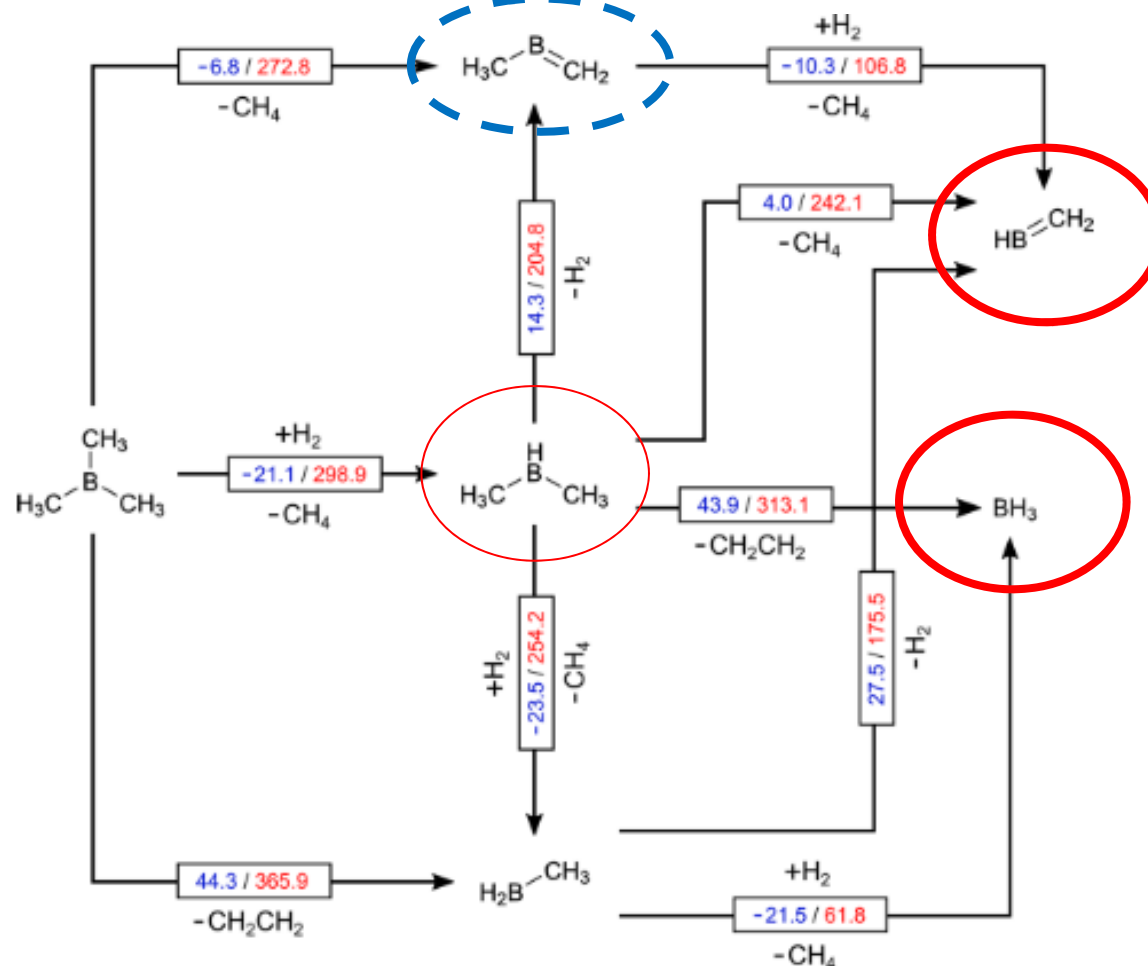Decomposition in Ar ambient at 800 °C



Imam, M.; Souqui, L.; Herritsch, J.; Stegmüller, A.; Höglund, C.; Schmidt, S.; Hall-Wilton, R.; Högberg, H.; Birch, J.; Tonner, R.; Pedersen, H. Gas Phase Chemistry of Trimethylboron in Thermal Chemical Vapor Deposition. *J. Phys. Chem. C* **2017**, *121*, 26465–26471.

# Boron-Carbon films from Trimethylboron

Decomposition
pathway in $H_2$



Imam, M.; Souqui, L.; Herritsch, J.; Stegmüller, A.; Höglund, C.; Schmidt, S.; Hall-Wilton, R.; Högberg, H.; Birch, J.; Tonner, R.; Pedersen, H. Gas Phase Chemistry of Trimethylboron in Thermal Chemical Vapor Deposition. *J. Phys. Chem. C* **2017**, *121*, 26465–26471.

# Boron-Carbon films from Trimethylboron

Decomposition
pathway in H$_2$

- - - -   in Ar and H$_2$
———   in H$_2$

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# Motivation for this work

- Observation in hydrogen ambient at 700 °C and 5000 Pa

| Deposition time (min) | Thickness (nm) |
|---|---|
| 30 | N/A |
| 90 | 77 |
| 270 | 84 |

Imam, M.; Souqui, L.; Herritsch, J.; Stegmüller, A.; Höglund, C.; Schmidt, S.; Hall-Wilton, R.; Högberg, H.; Birch, J.; Tonner, R.; Pedersen, H. Gas Phase Chemistry of Trimethylboron in Thermal Chemical Vapor Deposition. *J. Phys. Chem. C* **2017**, *121*, 26465–26471.

# Experimental conditions

- Observed in $H_2$, not in Ar

- Observed at 700 °C, but not at 800 °C

- Saturated thickness: ≈ 100 nm at 5000 Pa and 700 °C
  (usually between 70 and 150 nm)
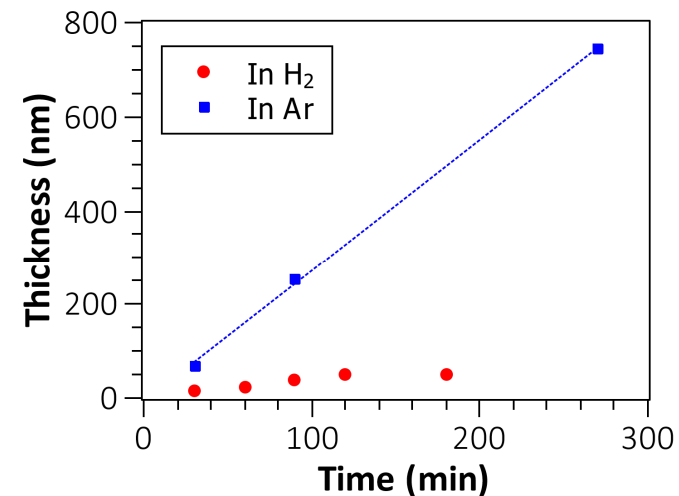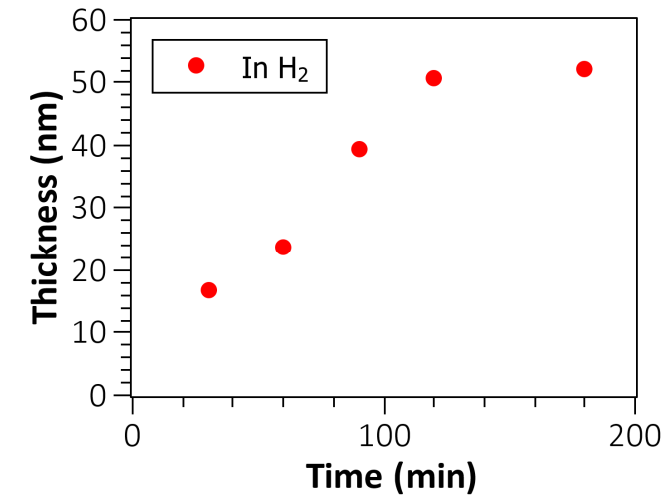
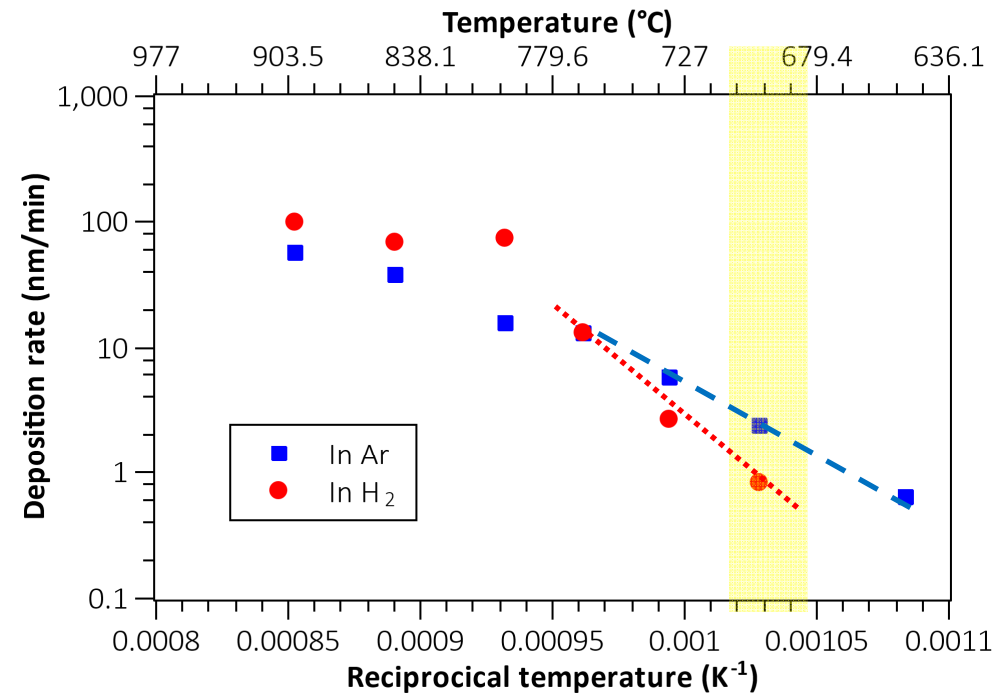# Arrhenius plots for TMB pyrolysis

- in Ar:
  - $E_A$: 202.8 kJ/mol
  - K: 1.96 x $10^{11}$

- in $H_2$:
  - $E_A$: **341.8** kJ/mol
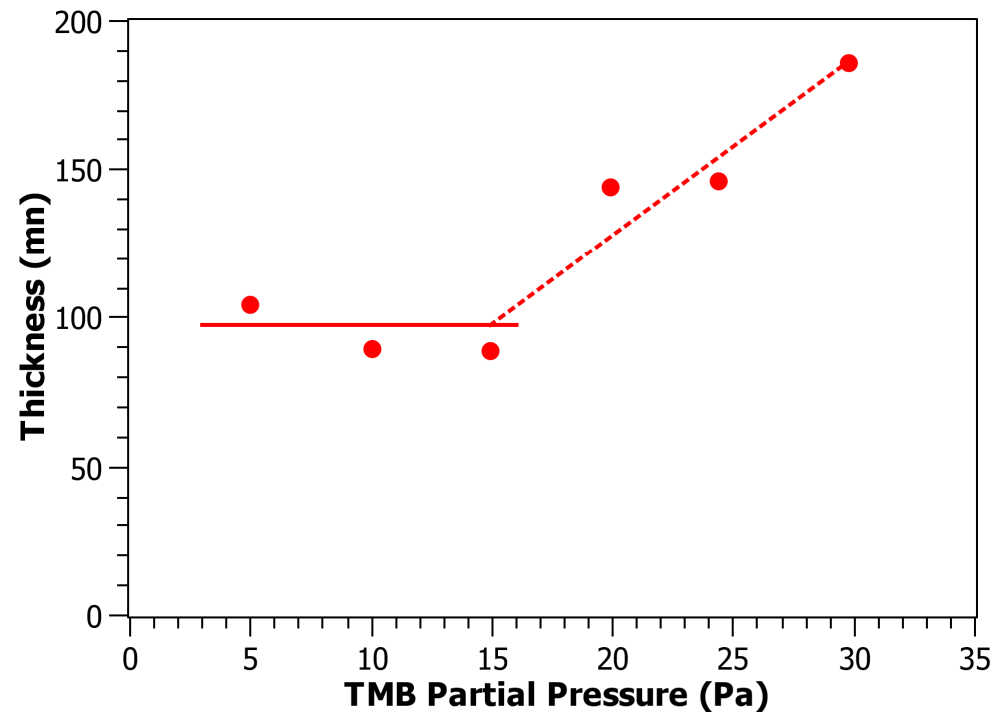  - K: 1.78 x $10^{18}$
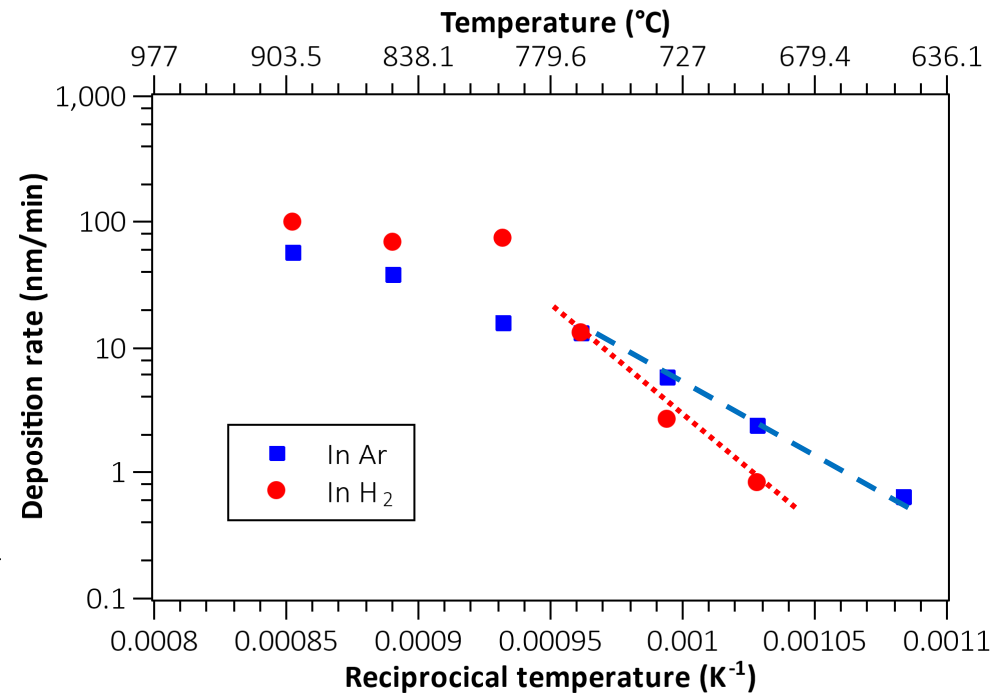
# Arrhenius plots for TMB pyrolysis

- Deposition regime:

  - Kinetically limited-regime:

  $\Rightarrow$ Growth rate depends only on:

    - precursor partial pressure

    - number of free deposition sites

# Respective effects of TMB and H$_2$

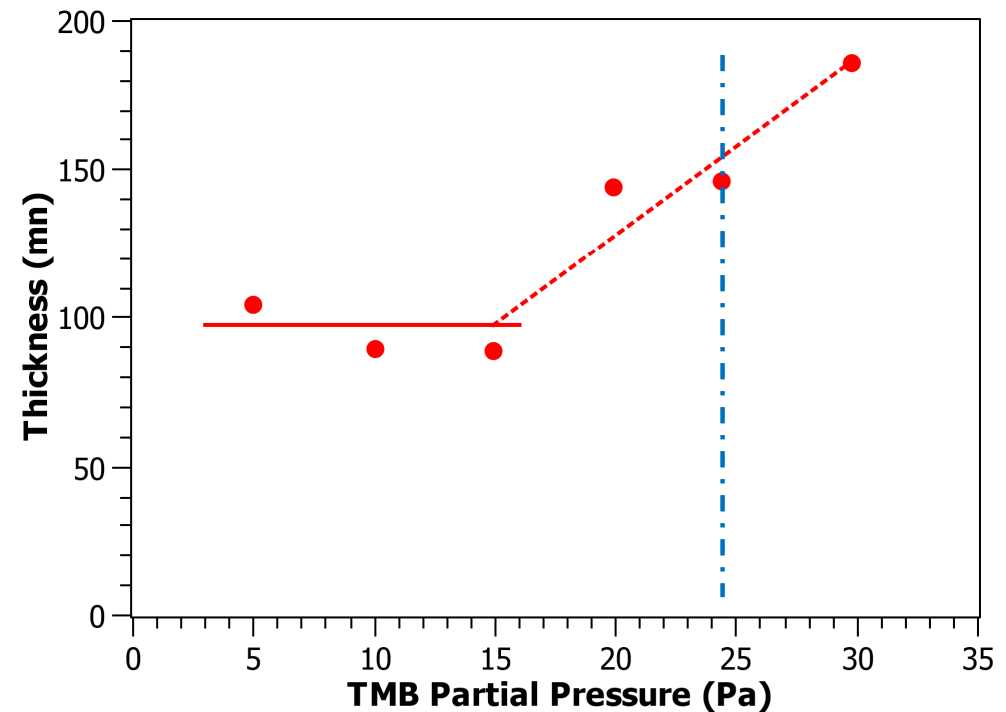- Deposition at constant hydrogen pressure (5000 Pa H$_2$, 60 min): two regimes

  – Saturated growth below 15 Pa TMB

  – Linear behaviour above 15 Pa TMB

# Respective effects of TMB and H$_2$

- Deposition at constant hydrogen pressure (5000 Pa H$_2$, 60 min) : two regimes

  – Saturated growth below 15 Pa TMB
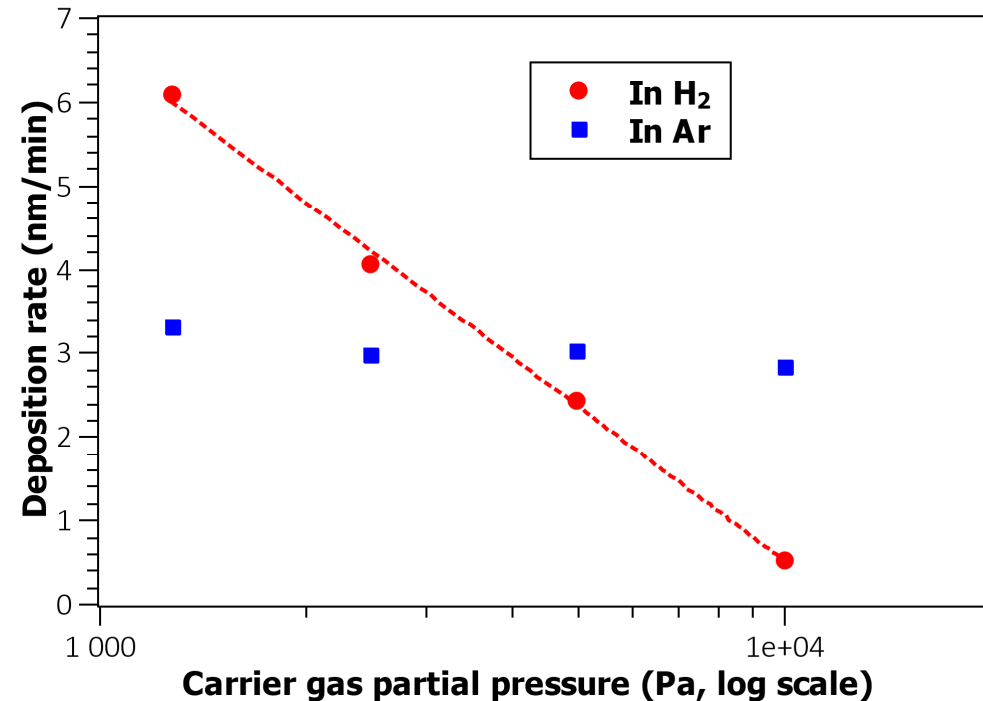
  – Linear behaviour above 15 Pa TMB



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# Respective effects of TMB and H$_2$

- Deposition at constant TMB pressure (24.5 Pa, 60 min)
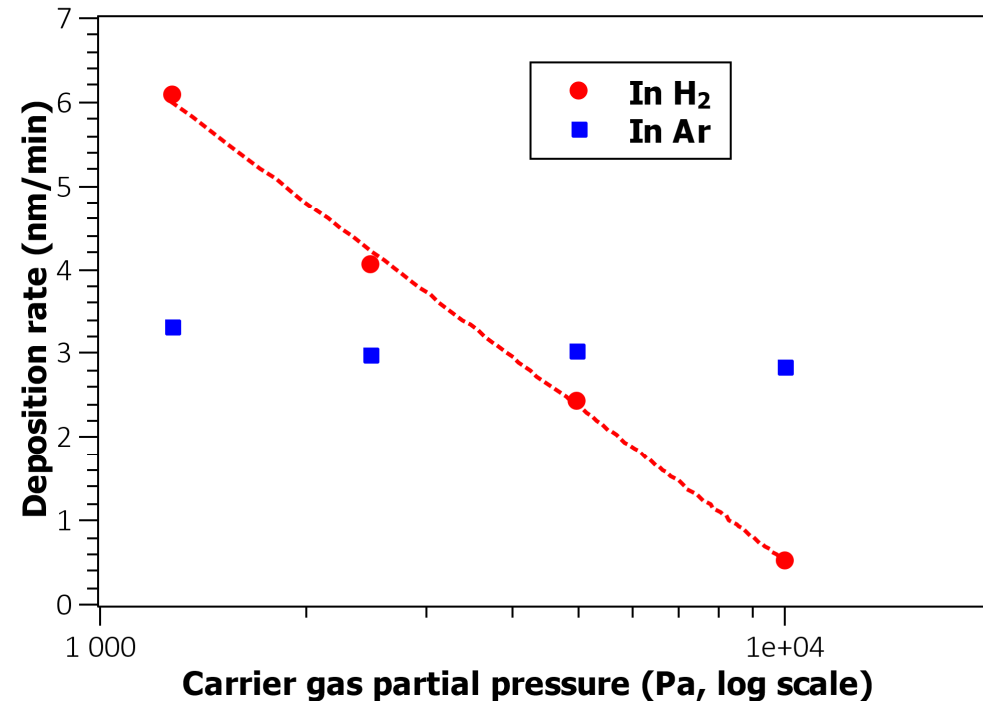
$$P_{H_2} = \frac{F_{H_2}}{\left(F_{H_2} + F_{TMB}\right)} P \approx P$$

$$P_{TMB} = \frac{F_{TMB}}{\left(F_{H_2} + F_{TMB}\right)} P$$

$$\approx \frac{F_{TMB}}{F_{H_2}} P$$



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# Respective effects of TMB and H$_2$

- Deposition at constant TMB pressure (24.5 Pa, 60 min)

  – In Ar: constant

  – In H$_2$: growth rate decreasing prop. to log(P$_{H2}$)

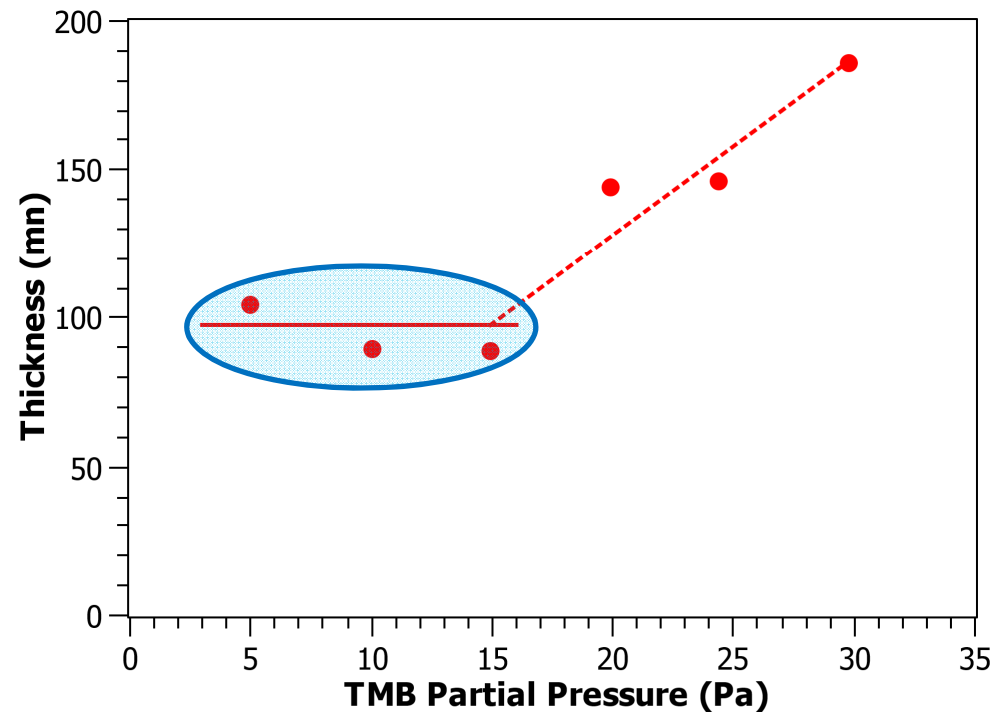  – This was also observed for 120 min deposition

# Hypotheses

- Non-sticking/reacting products of decomposition in $H_2$

- Etching

- Surface poisoning

- Competitive adsorption

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# Possible explanation

- Non-sticking products?

Can explain growth
rate drop

Cannot explain the
behaviour observed by
changing $P_{TMB}$

# Possible explanation

- Hydrogen etching?

| Process | Film thickness (nm) |
|---|:---:|
| 60 min growth | 146.3 |
| 30 min growth + 60 min $H_2$ exposure + 30 min growth | 156.3 |

The thickness is same within experimental error

    => Etching cannot explain the phenomenon

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# Possible explanation

- Surface poisoning?

| Process | Film thickness (nm) | Expected (nm) |
|---|---|---|
| 180 min at 3.25 Pa TMB<br>+ 60 min at 27 Pa TMB | 500 | ≈ 100 |

Growth can be resumed after exposure 3 hours deposition in conditions that afford inhibited growth

=> The surface did not become inactive

# Possible explanation

- Dynamic coverage by hydrogen:
  – Possible considering a Temkin adsorption isotherm
  – Heterogeneous surface

$$GR = (1 - \theta_T)GR_0$$

$$GR = \left(1 - \frac{RT}{b}\ln(A * P_{H_2})\right)GR_0$$

Temkin, M. I.; Pyzhev, V. Kinetics of ammonia synthesis on promoted iron catalyst, *Acta Phys. Chim. USSR*, **1940**, 12, 327–356.
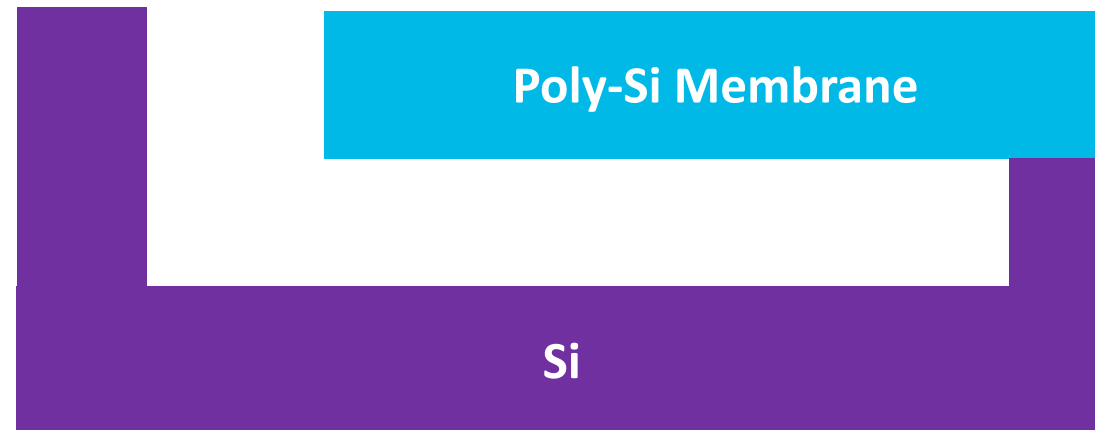
# Application to high aspect ratios

- Deposition in 60:1 aspect ratio vias

- 30 nm thick on top

- Reach bottom without clogging
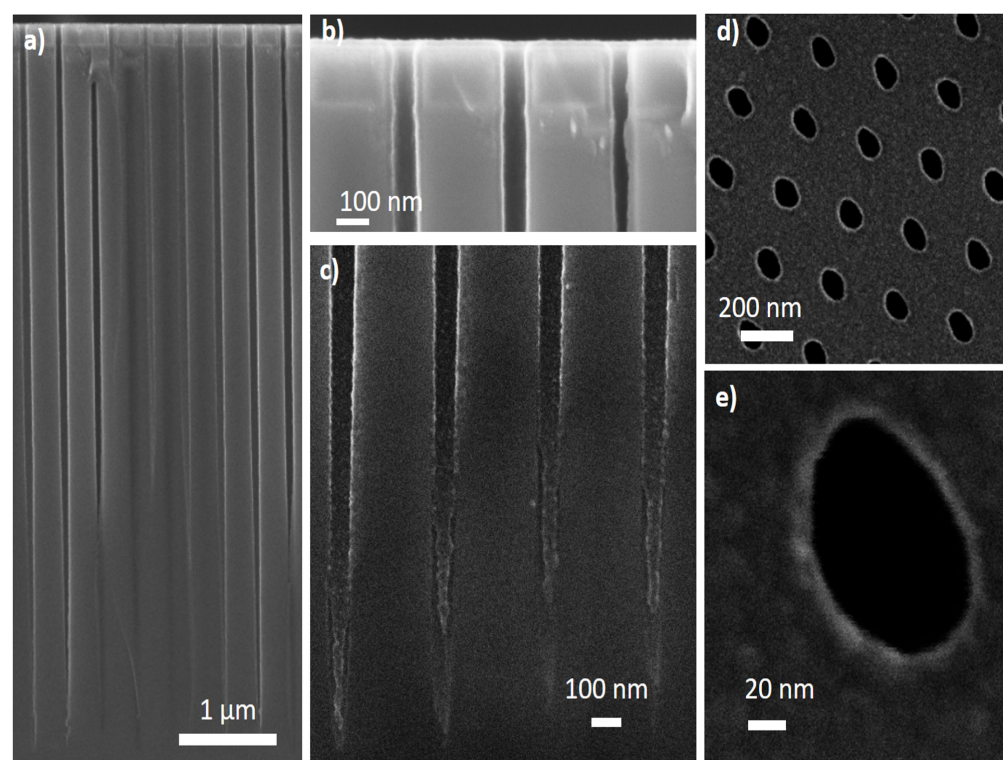
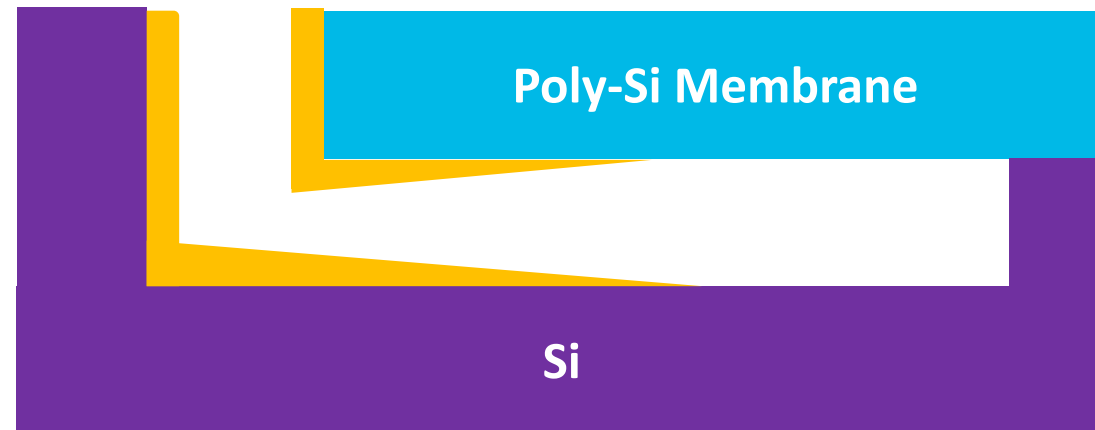# Application to high aspect ratios

- Deposition in lateral high aspect ratio structures (up to 10048:1, 500 nm gap)



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# Application to high aspect ratios

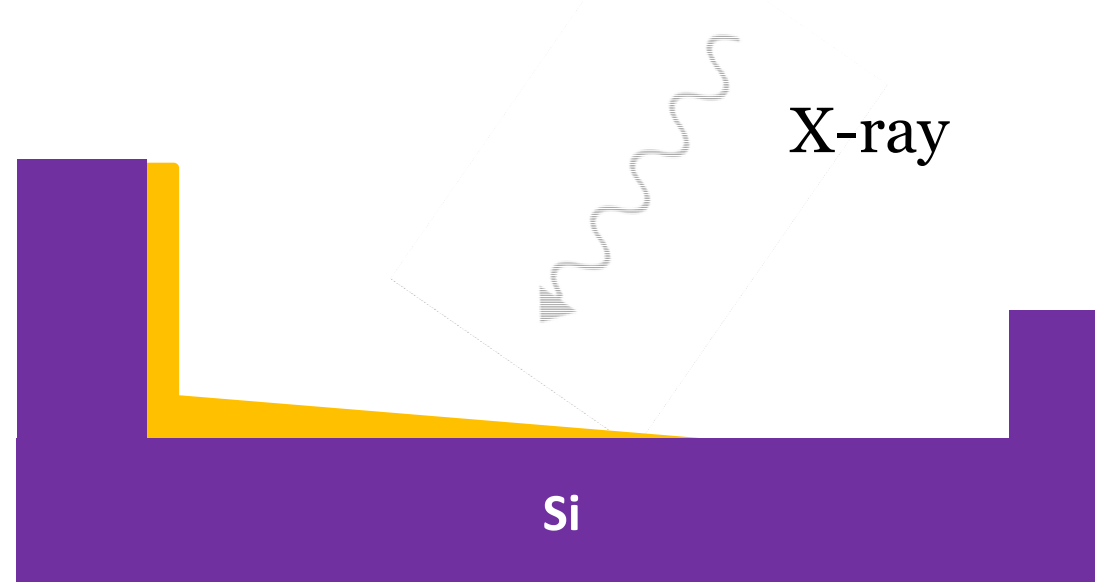- Deposition in lateral high aspect ratio structures (up to 10048:1, 500 nm gap)



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# Application to high aspect ratios

- Deposition in lateral high aspect ratio structures (up to 10048:1, 500 nm gap)

**Si**

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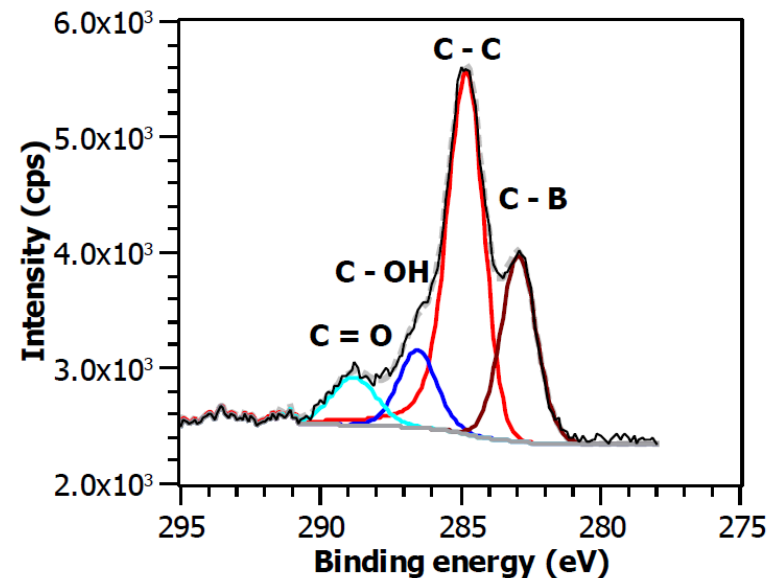
# Application to high aspect ratios

- X-ray photo electron spectroscopy (XPS) in lateral high aspect ratio structures (up to 10048:1, 500 nm gap)

X-ray

Si

# Application to high aspect ratios

- Deposition in 10048:1 lateral high aspect ratio structures (500 nm gap)

- XPS at AR ≈ 2500:1 :

    – B/C = 0.45 in trench, (0.5 outside)

# Conclusion

- We show inhibition of B-C film growth in $H_2$, 700 °C and 5000 Pa

- We propose that inhibition is due to competitive adsorption between TMB and $H_2$ and that $H_2$ adsorption can be described by a Temkin isotherm

- We can deposit B-C thin films in deep features at these conditions

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# Acknowledgments

- Pedersen group and functional materials unit at LiU



- Financial support

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# Thank you for your attention!

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