EUROPEAN
SPALLATION
SOURCE

^{10}B based thin films for next generation of neutron detectors using different deposition techniques

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LiU EXPANDING REALITY

European Spallation Source (ESS)

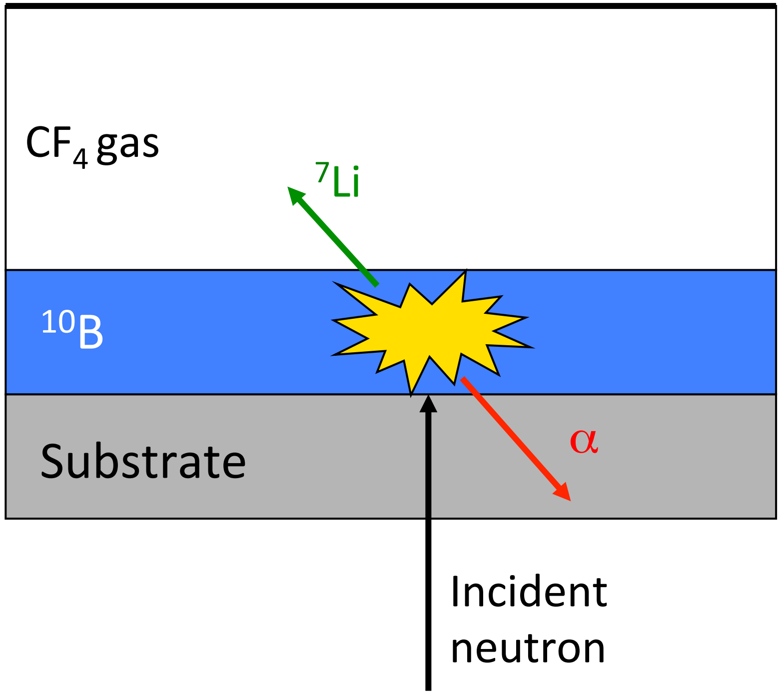
- **ESS** in Lund, Sweden - the world's leading neutron source for the study of materials
- Neutron detectors based on the isotope ^{10}**B** instead of ^{3}He
- The first neutrons and 7 instruments will be produced in 2019, the full baseline suit of 22 instruments in 2025

Neutron detection using ^{10}B

^{10}B has slightly less neutron absorption cross section compared to ^{3}He

$^{10}B + n \rightarrow {}^{7}Li + \alpha + \gamma$ (94 %)
$^{10}B + n \rightarrow {}^{7}Li + \alpha$ (6 %)

^{nat}B contains
- 80 at.% ^{11}B
- 20 at.% ^{10}B



Boron containing thin film B_4C

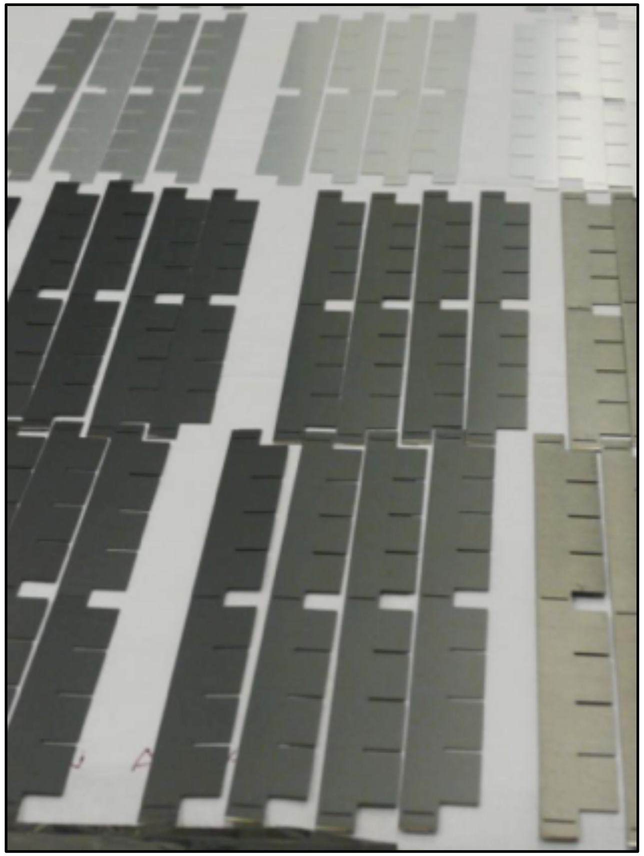
- Elemental B:

  - Bad oxidation resistance

  - Poor electrical conductivity

- B_4C:
  - Excellent wear resistance, thermally and chemically stable
  - Better electrical conductivity
  - Easy to deposit with DC magnetron sputtering

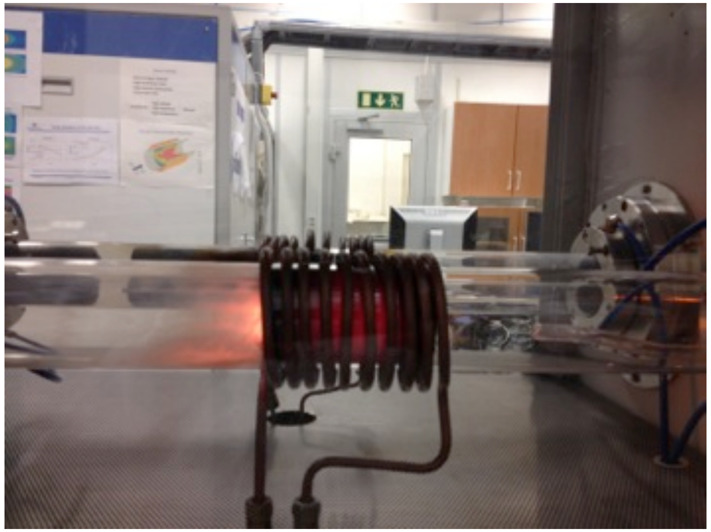
Demands on the thin films



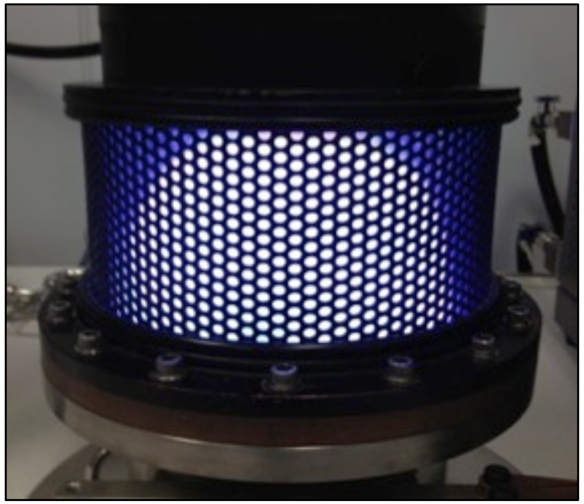
- Thickness > 1 µm
- 1- or 2-side coated substrates (neutron transparent)
- Good adhesion and low stress
- No demands on the crystallinity
- High density
- Minimal amount of impurities

Deposition techniques in this project

DC magnetron sputtering

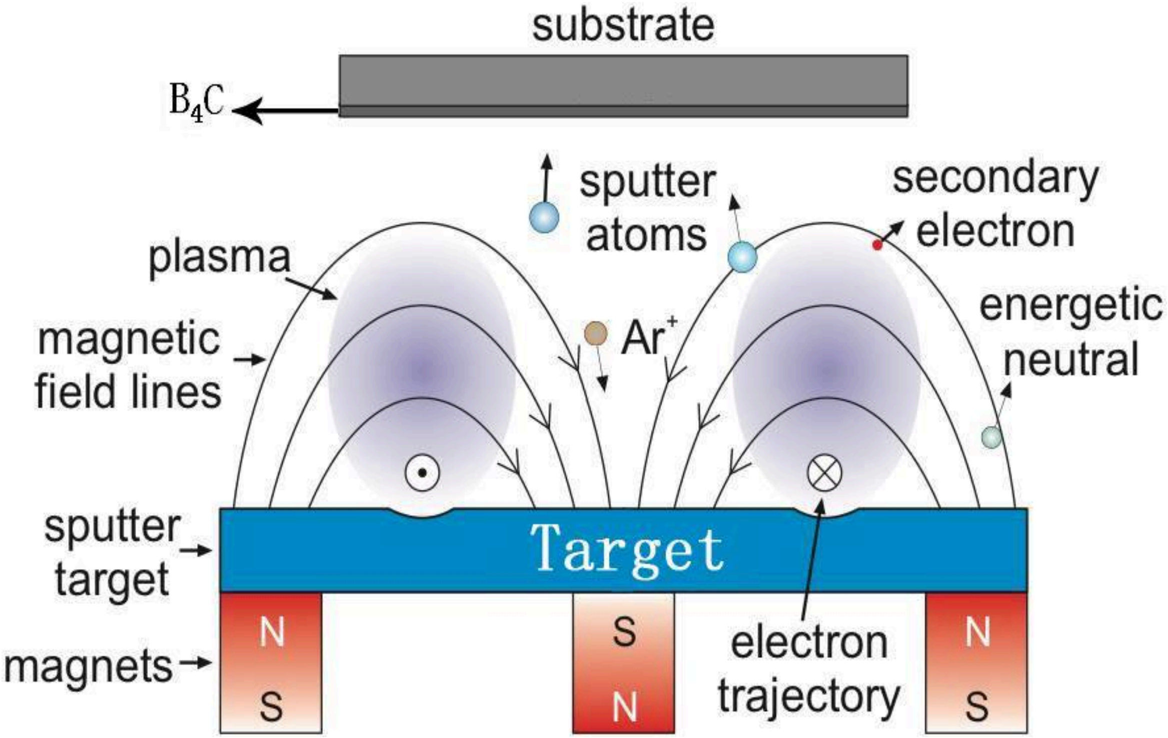


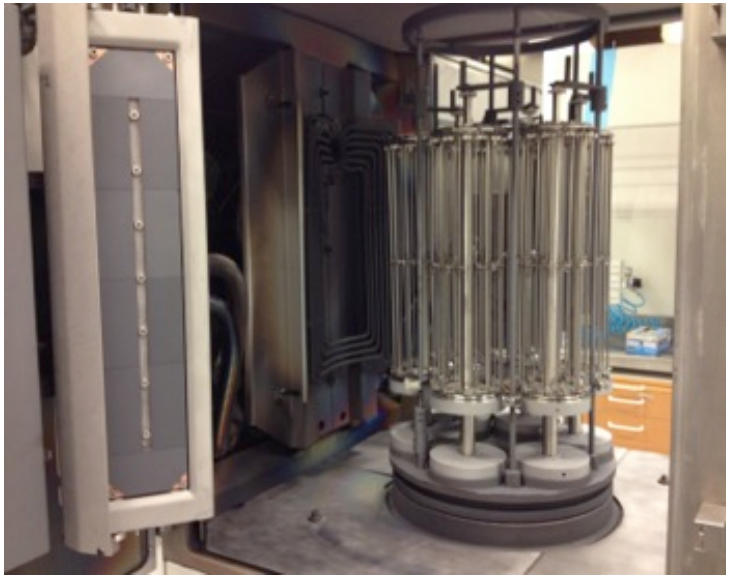
Thermally activated CVD



Plasma enhanced CVD (PECVD)

DC magnetron sputtering of $^{10}B_4C$ (PVD)

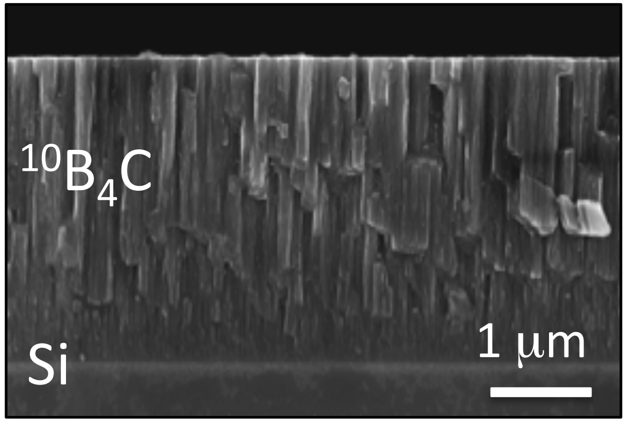




LiU deposition system

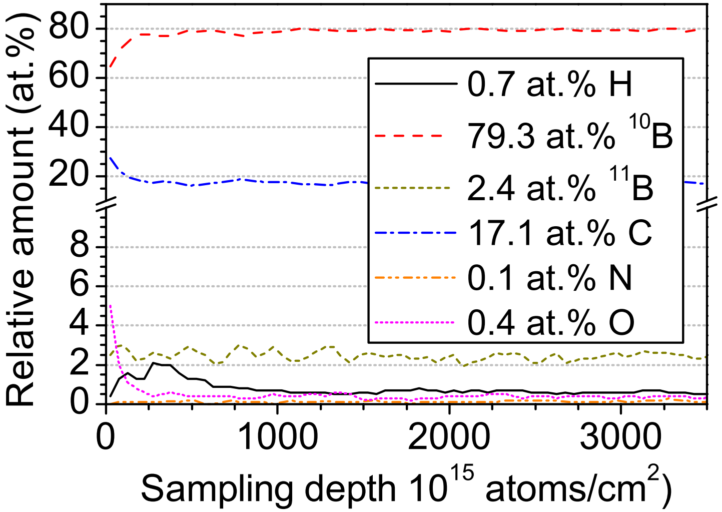
Deposition in an industrial system, CemeCon CC800/9

SEM cross sectional image

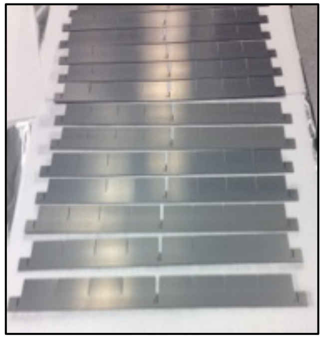


Required property	Result	OK?
Good adhesion	> 1 μm on Al, Si, Al_2O_3, etc	☺
Low residual stress	0.09 GPa at 1 μm $^{10}B_4C$	☺
High density	2.45 g/cm^3, 97% of bulk*	☺
High ^{10}B content	79.3 at.% of ^{10}B	☺
Low impurities	H +N + O only ~1 at.%	☺

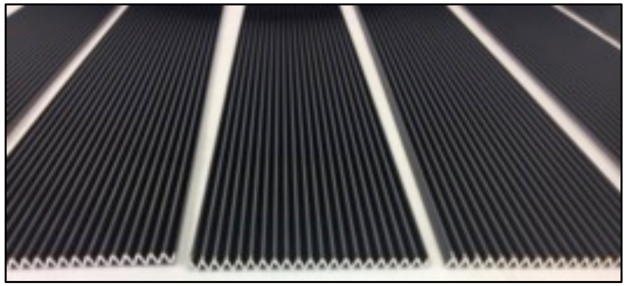
Film composition-ERDA



Patent SE 535 805 C2
C. Höglund et al., J. APPL. Phys. **111**, 104908 (2012)
*O. Knotek et al. Surf. Coat. Tech. **1997**, 91, 167



Coatings on Al blades



Coatings for different prototype

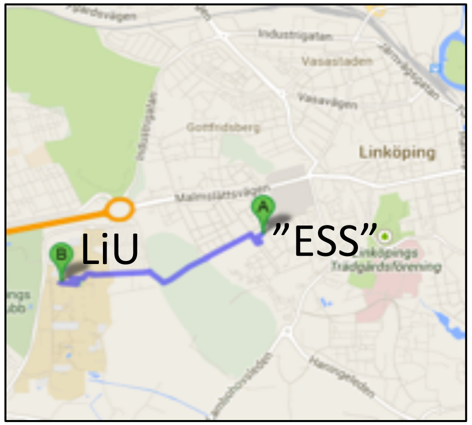
ESS coating facility in Linköping

9/2013: New deposition system ordered
- Only for $^{10}B_4C$ coating for neutron detectors
- Covers needs of the ESS (6000 m^2)

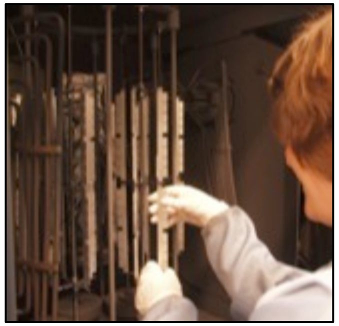
4/2014: FAT documents signed

23 June-2014 - delivery date

2014-2016: Up-scaling - 1000 m^2/year



Staff:
1 engineer – 1 September start
1 technician (Q4, 2014)
Carina Höglund ~50%



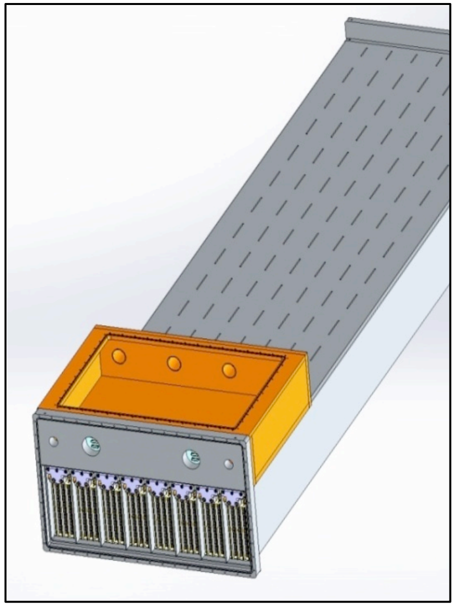
<u>Close collaboration with LiU:</u>

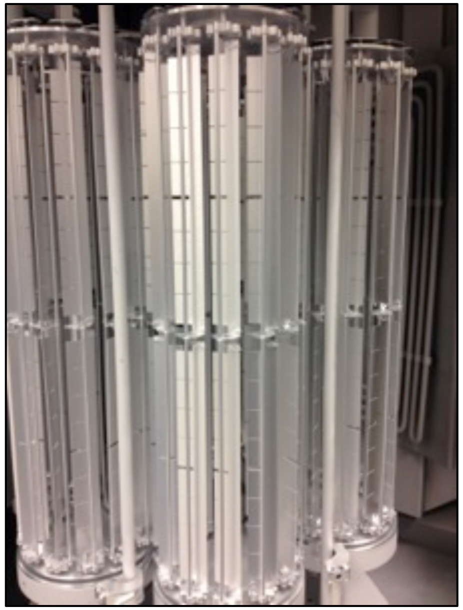
➔ <u>Research & competence</u>
- Sputtering, CVD, PECVD, …

➔ <u>Characterization</u>
-SEM, SIMS, XRD, ERDA,…

➔ <u>Upgraded LiU deposition system</u>
- Backup system

Demonstrator - IN5 segment





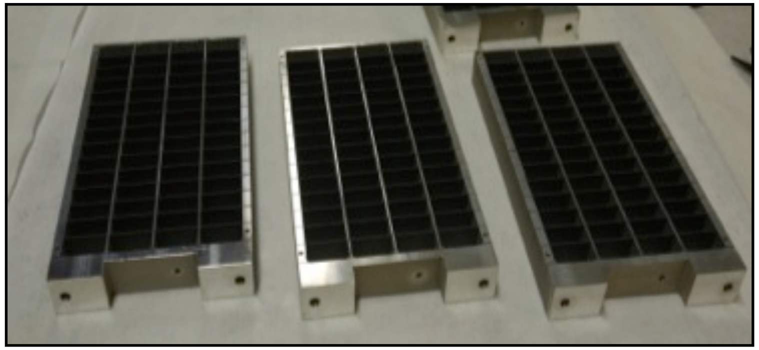
Mass production test!

Deadline September 2014

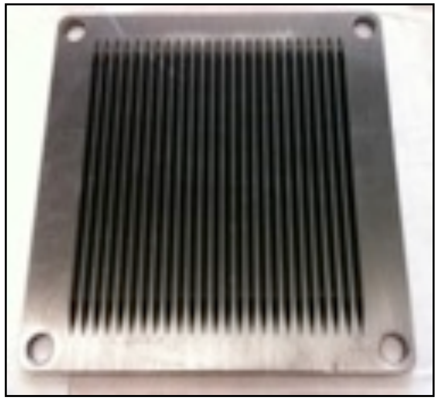
After this: Full scale detector!

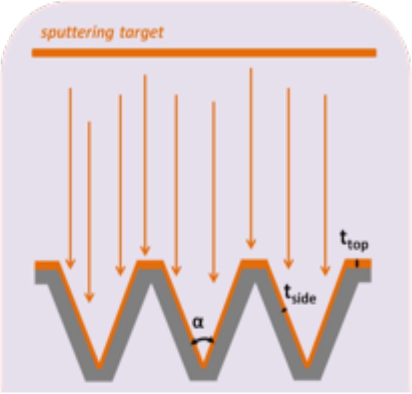
- Collaboration ESS – LiU – ILL
- 0.8 x 3 m^2 detector area
- 25 000 blades with $^{10}B_4C$, 103 m^2 in 45 days (up to 3.3 m^2/day)
- 0.75, 1 and 1,5 μm $^{10}B_4C$ coatings + 1 without coating
- 50% Ni-plated / 50% low-α Al

Deposition using CVD



- Expected less stress in the films – less problems with adhesion
- Not line of sight deposition – detector parts can be coated assembled, also allows for more complex detector geometries
- It is possible to get different film stoichiometry, i.e., B_xC where $x > 4$





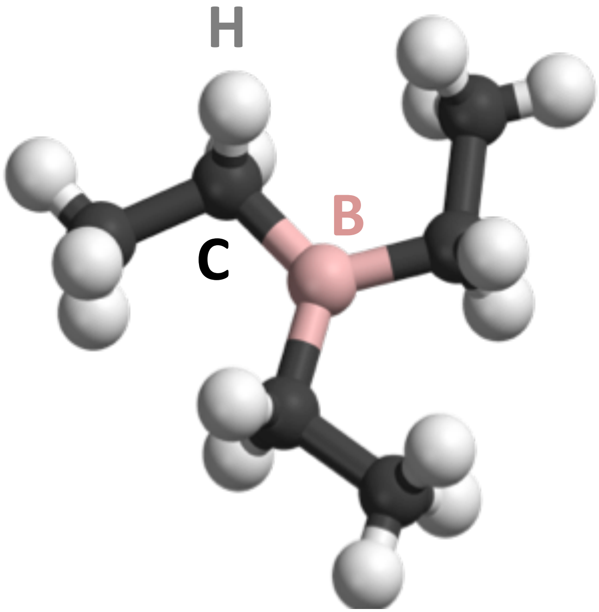
Traditional B_xC CVD

- Thermally activated CVD, 900-1300 °C Al melts at 660 °C
- Boron precursor BCl_3/BBr_3, produces HCl
- Carbon precursor: Light hydrocarbons typically CH_4 passive below 800 °C

Any alternatives?

U. Jansson, J-O. Carlsson, Thin Solid Films 124 p. 101 (1985).
L. G. Vandenbulcke, Ind. Eng. Chem. Prod. Res. Dev. 24 p. 568 (1985).
U. Jansson et al.Thin Solid Films 172 p. 81 (1989).
H. Vincent et al. Carbon 34 p. 1041 (1996).
J. Berjonneau et al. J. Electrochem. Soc. 153 p. C795 (2006).
Y. Liu et al. Appl. Surf. Sci. 255 p. 5729 (2009).

Alternative CVD route



TEB - TriEthylBoron

✓ Organoboranes, i.e. molecules with one or more B-C bonds:

Triethylborane (TEB) $B(C_2H_3)_3$
Trimethylborane (TMB) $B(CH_3)_3$
Tributyl borane (TBB) $B(C_4H_9)_3$

✓ Very reactive – lower process temperature

✓ Contain both B and C, no Cl

✓ TEB reported to be the best choice for low temperature boron-carbon films *

✓ Available as ^{10}B enriched

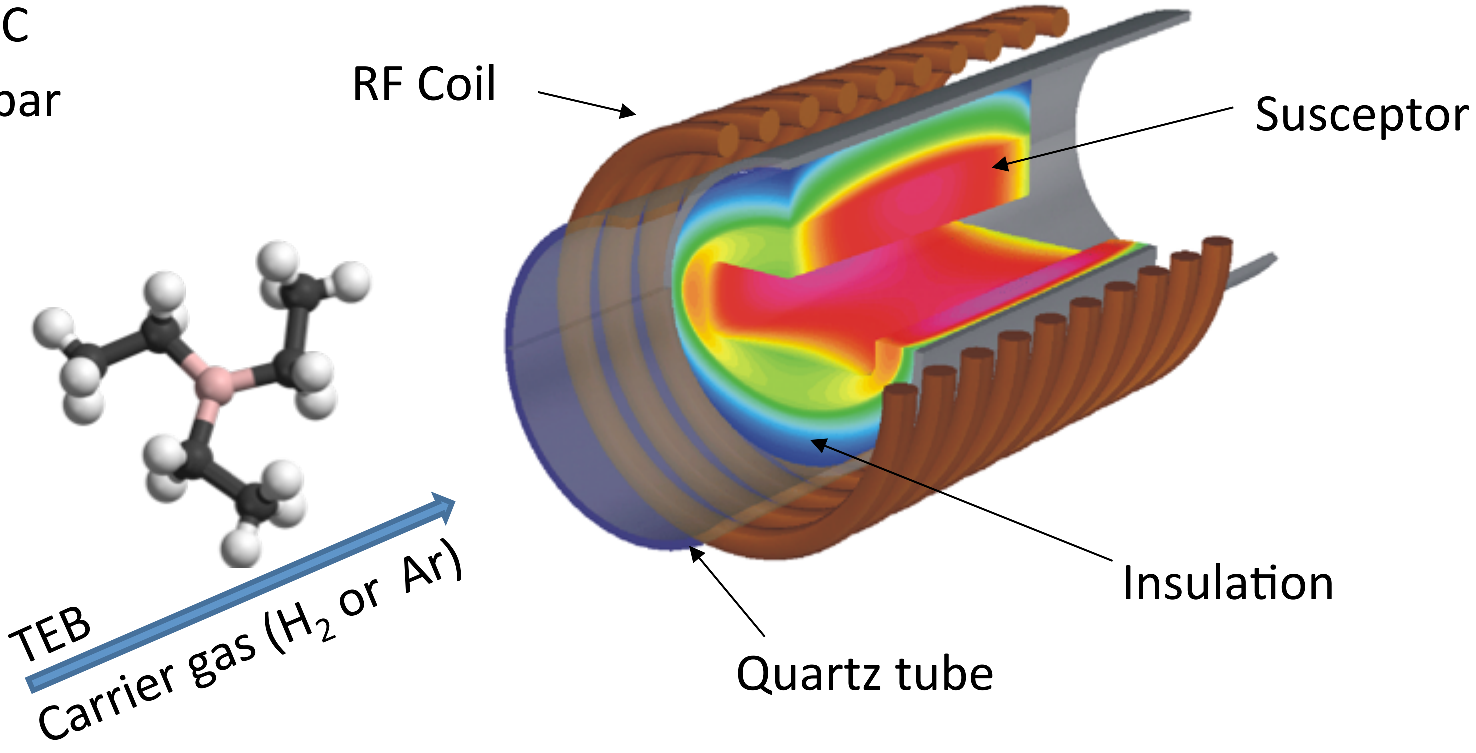
* J. S. Lewis et al. Mater. Lett. 27 p. 327 (1996)

Thermally activated CVD

Growth parameters:

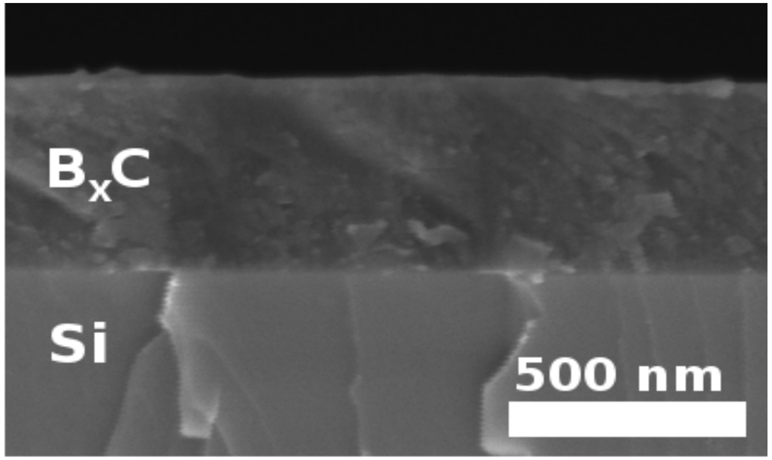
T = 400 – 600 °C

Pressure 50 mbar



Deposited films

- The films were found to be XRD amorphous, regardless of temperature and ambient
- Deposition rate at 600 °C:
  0.4 µm/h in H_2 ambient,
  1 µm/h in Ar
- Films with thickness of 0.5-1 µm adhere well to both Al blades and single crystal Si (100) surface

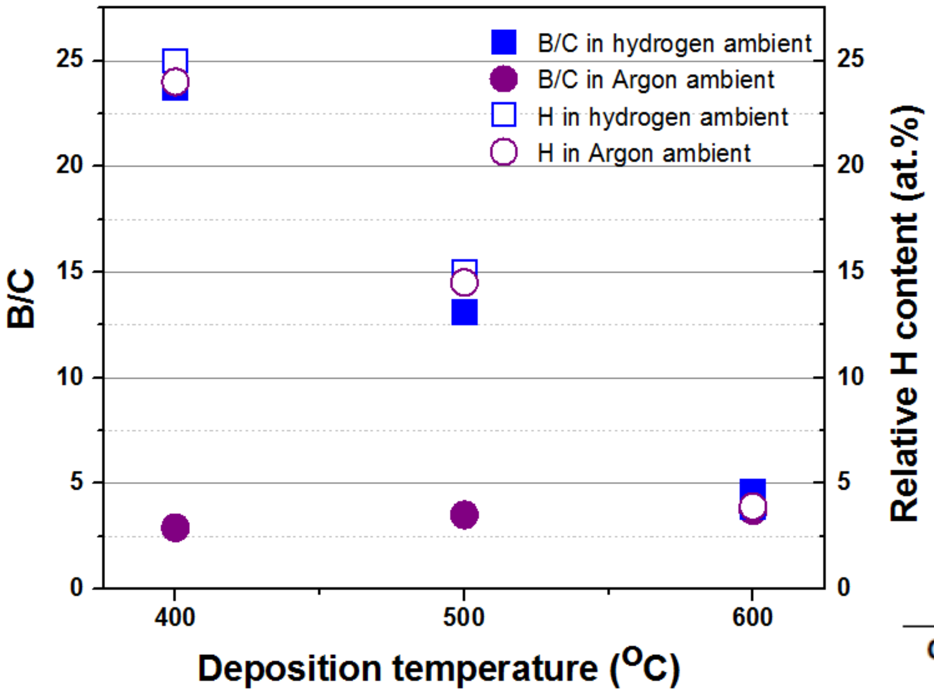


B_xC deposited at 600 °C in Ar

H. Pedersen et al. Chem. Vapor Deposition 18 p. 221 (2012)

Elemental composition & density

Elastic Recoil Detection Analysis (ERDA)



Suggested chemical reaction mechanism:
In hydrogen ambient:

- At low temperature TEB decomposed BH_3 and CH_4 -> high B/C
- At high temperature TEB decomposed BH_3 and C_2H_4 -> lower B/C

In argon ambient:

- TEB only decomposed to BH_3 and C_2H_4

Carrier gas	Deposition temperature (°C)	Density (g/cm^3)
H_2	400	1.16 ± 0.3
H_2	600	2.42 ± 0.05
Ar	500	1.85 ± 0.05
Ar	600	2.14 ± 0.05

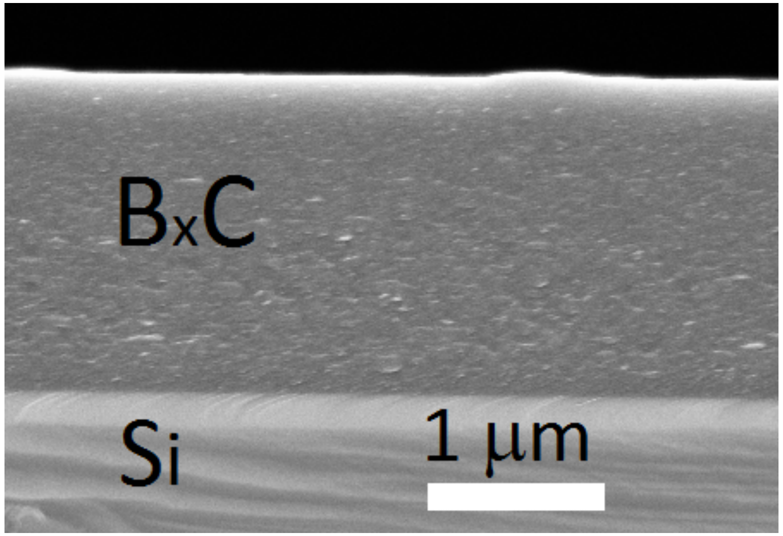
Bulk density for crystalline B_4C: **2.52 g/cm^3**

O. Knotek et al. Surf. Coat. Tech. **1997**, 91, 167

H. Pedersen et al. Chem. Vapor Deposition 18 p. 221 (2012

Deposition at high T using thermal CVD

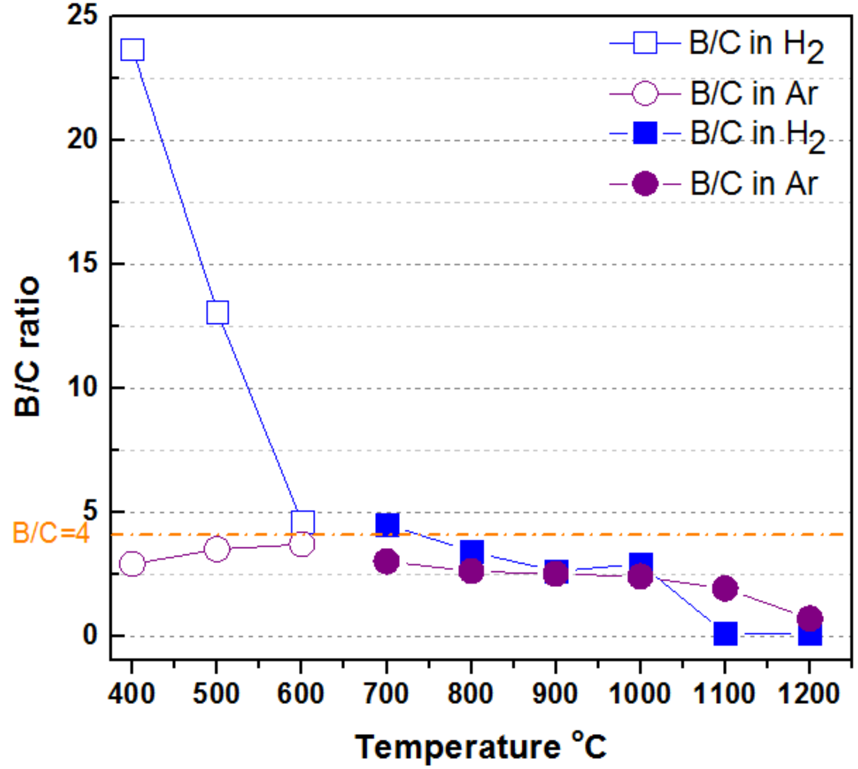
- Si (100) substrate
- Deposition temperature:
  700-1200 °C
- Good adhesion & dense film
- Deposition rate:
  1.39 µm/h in hydrogen
  955 nm/h in argon
  ambient at 700 °C
- Film density varies in 2.40 - 2.69 g/cm^3



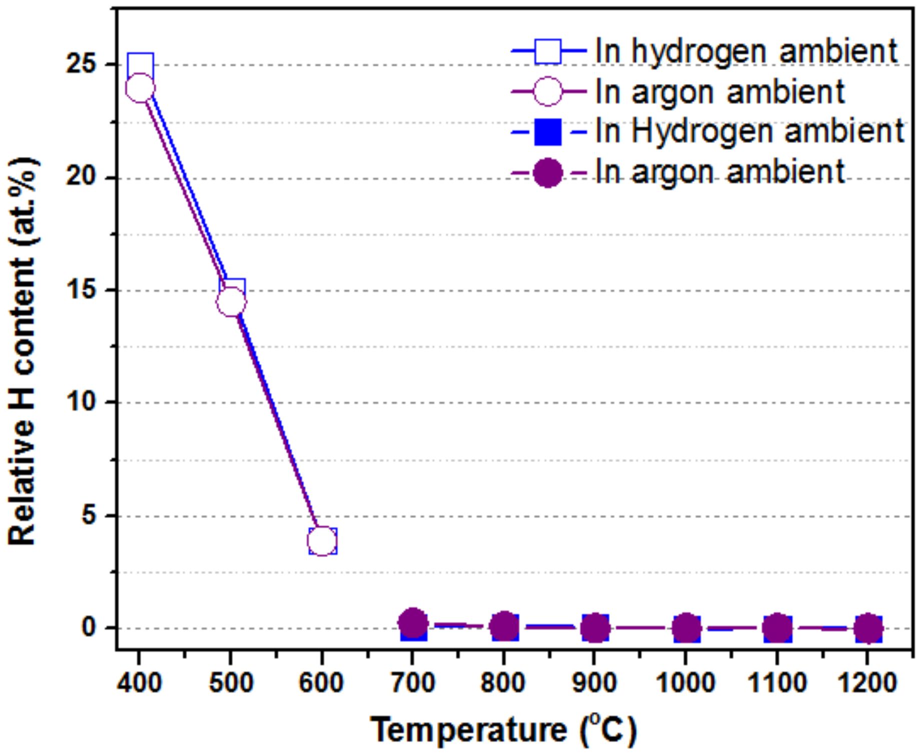
B_xC deposited at 800 °C in Ar

Elemental composition by ERDA

Precursor: $B(C_2H_3)_3$ (TEB)
Pressure: 50 mbar
Temperature: 700-1200 ^{o}C
Carrier gases: H_2 & Ar

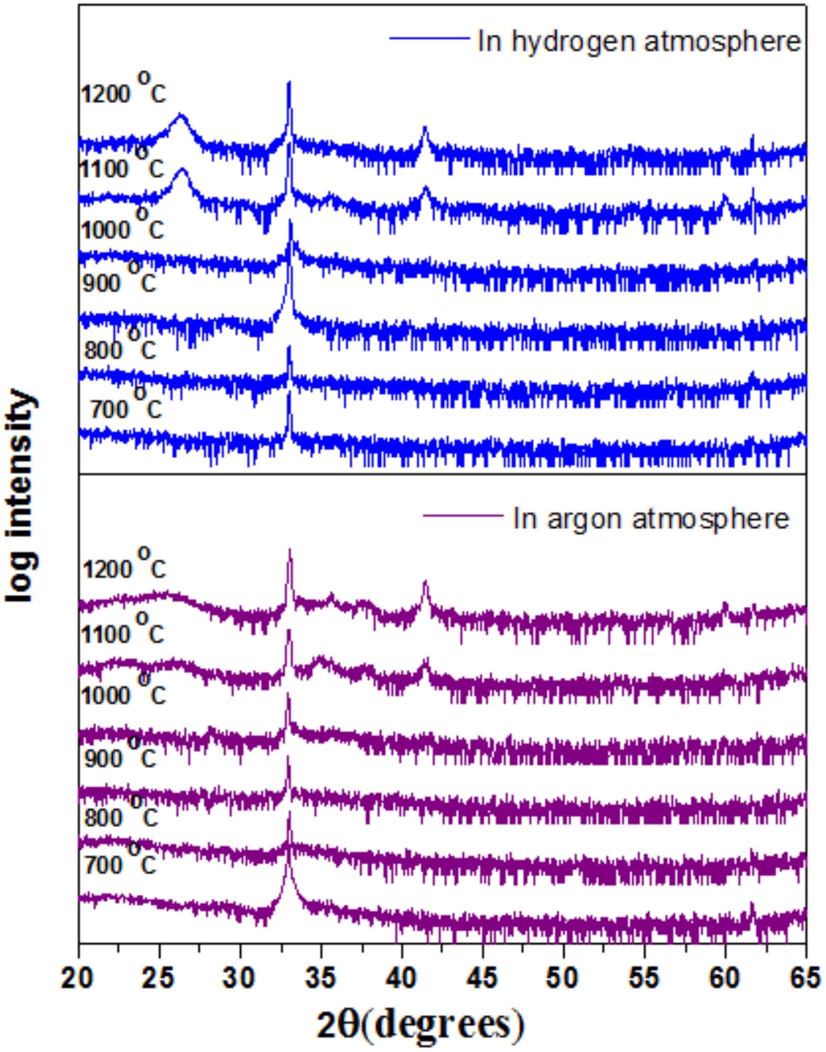


- B/C = 4.5 at 700 ^{o}C with 2.42 g/cm^3
- T > 1000 ^{o}C, mainly deposited C in H_2 ambient
- H < 0.3 at .%

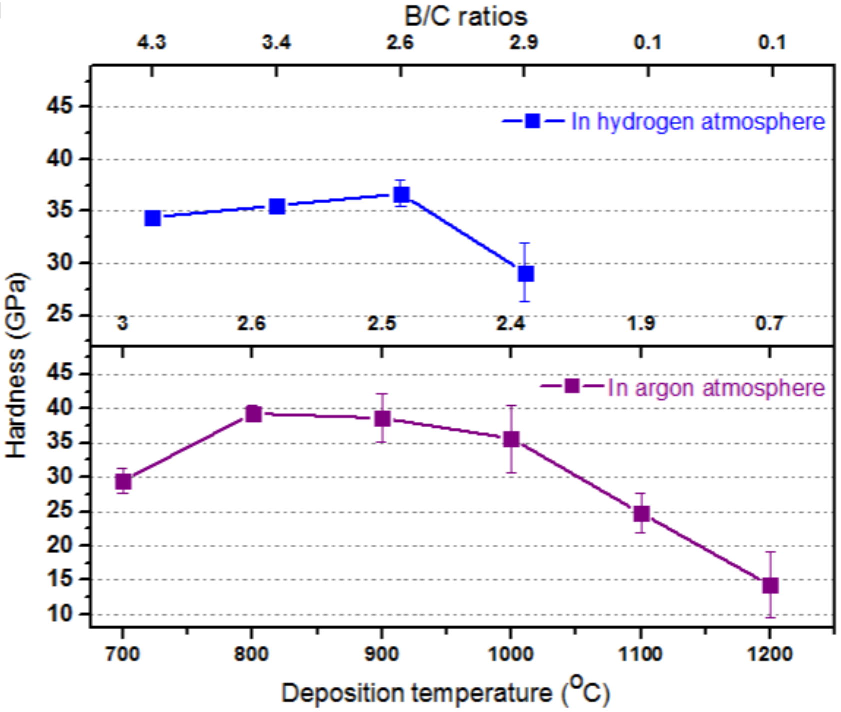


Structural and mechanical properties

X-ray diffraction



Hardness (Nano-indentation)



- T ≤ 1000 °C, films are amorphous
- > 1000 °C graphite in H_2 ambient
- Hardness 35 GPa and 33 GPa in Ar and H_2 ambient, respectively

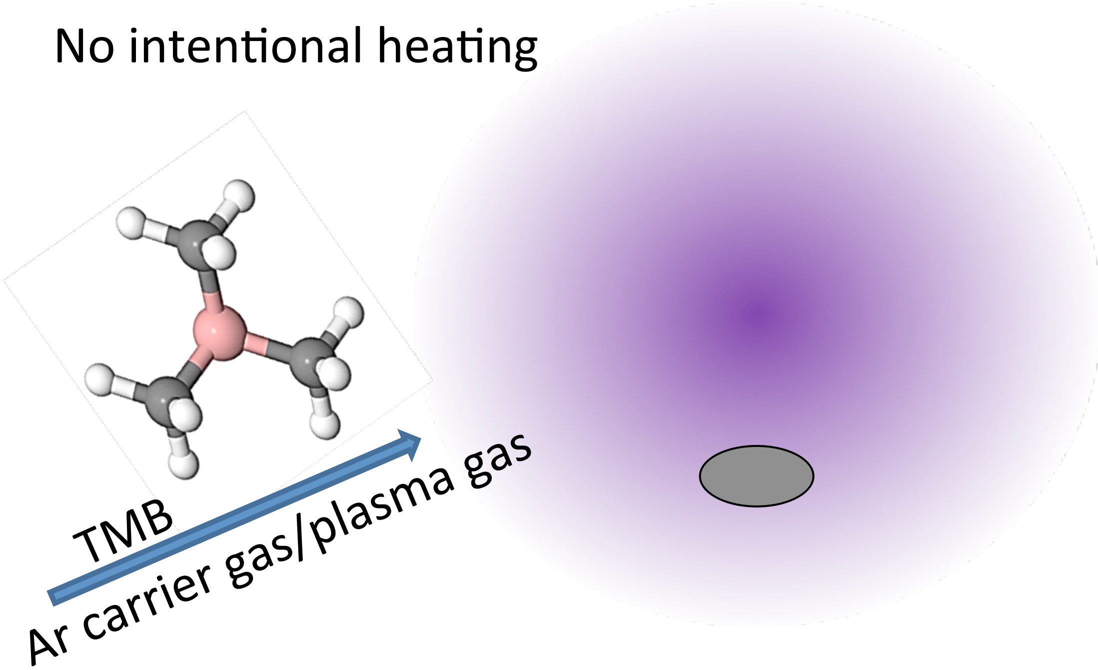
Plasma Enhanced CVD

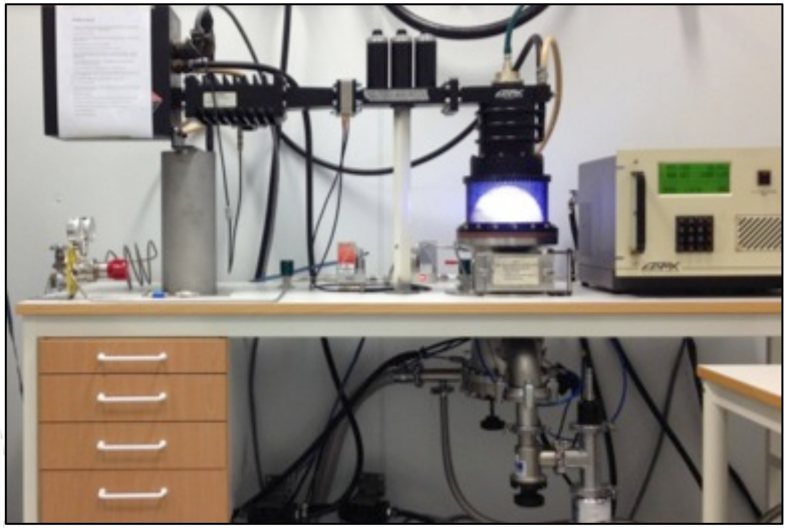
Usually first choice for low temperature CVD

Growth parameters:

Pressure 0.2 mbar

No intentional heating

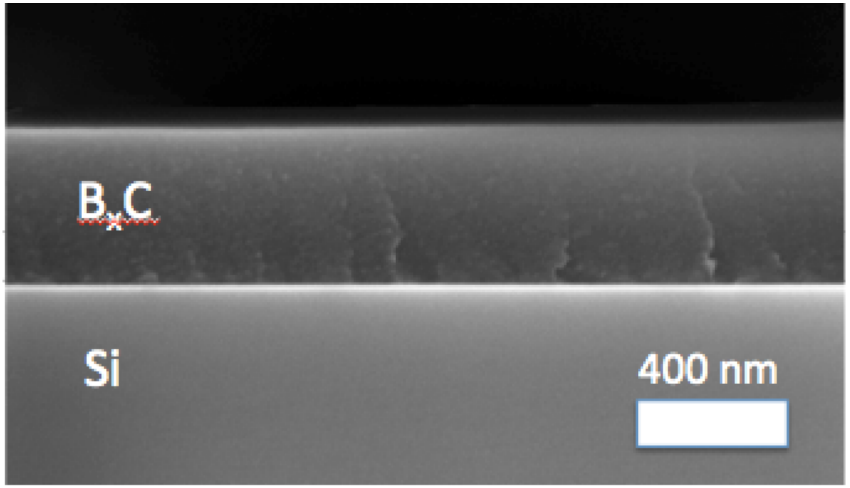




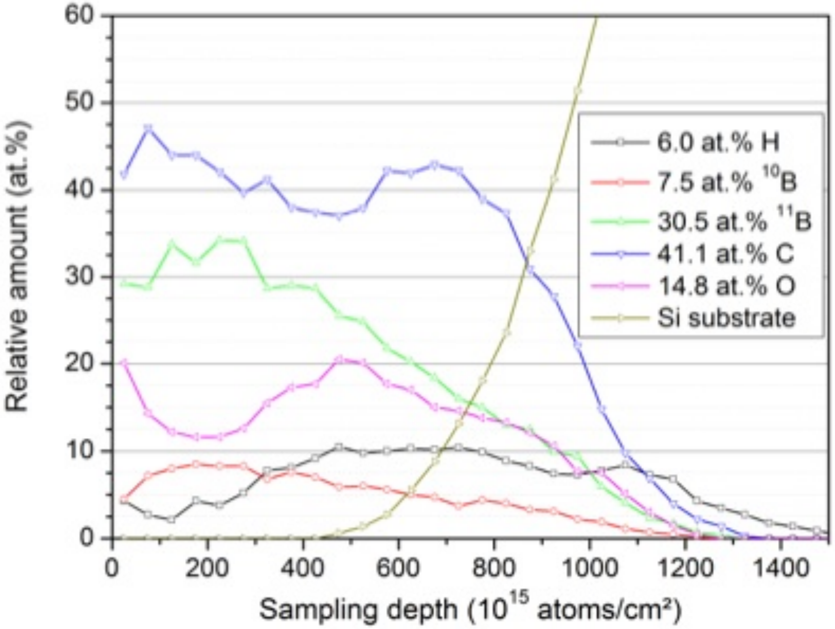
^{10}B enriched TMB is commercially available

Early results from PECVD

- Highest Deposition rate ~300 nm/h
- Smooth and dense films
- Film density: 1.25 - 1.49 g/cm^3



Film composition (ERDA)



Deposition parameter:
TMB 5 sccm
Ar 42 sccm
Power 2000 W

composition	Relative amount
B	38 at. %
C	41.1 at. %
H	6.0 at. %
O	14.8 at. %

B/C=1

Conclusions

- ^{10}B containing thin film based detectors – an alternative to ^{3}He detectors
- $^{10}B_4C$ thin films deposited by PVD, up to 3.3 m^2/day, dedicated machine will be around within a month
- Thermal CVD process of B_xC using TEB shows:

  B/C ~ 4.6, impurity level ~ 4 at.% at 600°C

  B/C= 4.3, impurity level ~ 0.1 at.% at 700 °C
- PECVD using TMB shows promising early results and is under development

Acknowledgements

Knut och Alice Wallenbergs Stiftelse

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Thank you for your attention!

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