The fundamental role of ion bombardment for the synthesis of c-BN thin films

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Outline

- BN phase formation diagrams
- Prediction by the Cylindrical Thermal Spike Model
- Experiments
- Ion energy limits for c-BN growth
- Comparison with ion irradiation experiments
- Puzzling new results
- Summary

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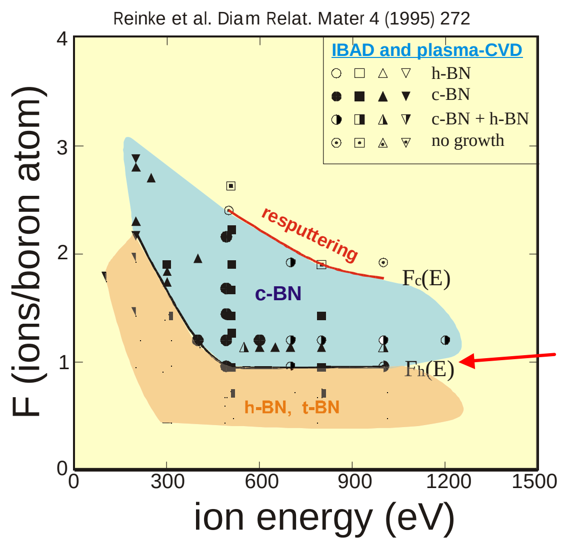
BN phase formation diagram for IBAD and plasma CVD



Nucleation threshold (momentum transfer criterion F ? $E_{ion}^{-1/2}$)

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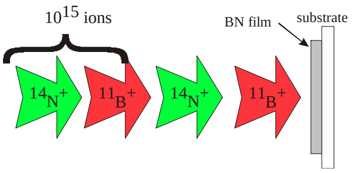
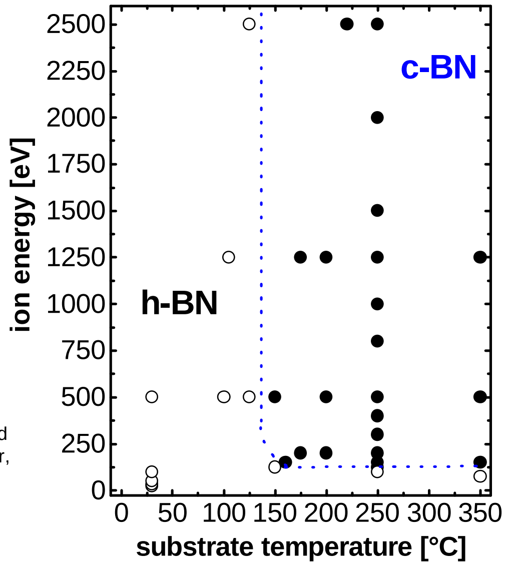
BN phase formation diagram for mass selected ion beam deposition (MSIBD)





Nucleation thresholds:
T = 150 °C, E ? 125 eV

Feldermann et al., in Hard coatings based on Borides, Carbides & Nitrides, A. Kumar, Y.Chung, R.W.J. Chia (eds.), (TMS, Warrendale, 1998), p.143

Ronning et al., DRM 9 (2000) 1767

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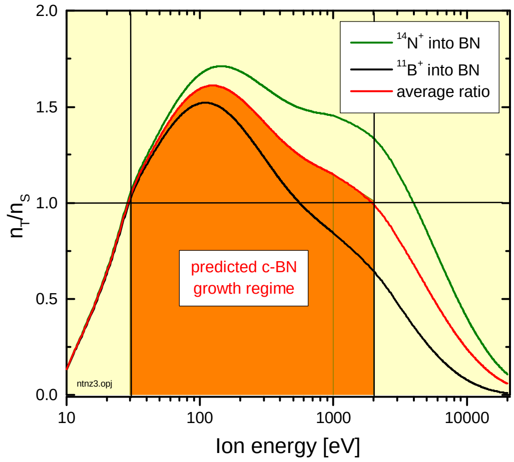
Prediction by the cylindrical thermal spike model

Hofsäss et al., Appl. Phys. A 66 (1998) 153

Parameter n_T/n_S for B^+ and N^+ ions in c-BN



n_T = # rearrangements
n_S = # atoms in spike volume

Predicted c-BN growth regime:
n_T/n_S >1 (Thermal spike dominates)

30 eV < E_{Ion} < 4 keV

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Nucleation conditions vs. growth conditions

Temperature threshold:

Mirkarimi et al. DRM 5 (1996) 1295: c-BN growth at 75 °C
Feldermann et al., APL 74 (1999) 1552: c-BN growth at room temperature

Ion energy threshold:

McKenzie et al., NIM 196 (1995) 90
Yoshida et al., APL 70 (1997) 946
Litvinov et al.,APL 71 (1997) 19
Hahn et al., SCT 92 (1997) 129
Bewilogua et al. DRM 5 (1996) 1130

Nucleation threshold: 65 - 200 eV
Growth threshold: 45 -165 eV

→ E^n_{th} ? E^g_{th} ? 20 ? 40 eV

Our experiments

„Nucleation“ layer: T_S = 250 °C, E_{Ion} = 600 eV, Q = 0.2 C
„Growth“ layer: T_S = 250 °C, E_{Ion} = 50, 75,100 eV, Q = 0.1 C

Nucleation threshold: 125 eV
Growth threshold: 75 eV

→ E^n_{th} ? E^g_{th} ? 50 eV

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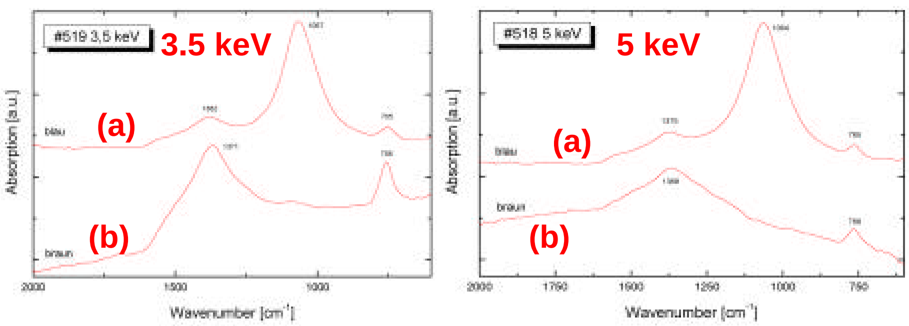
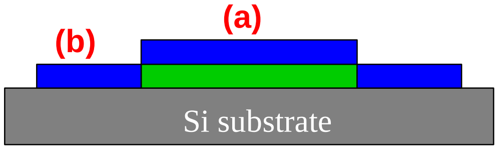
High energy limit of c-BN growth: experiments with E_{Ion} ? 5 keV

Hofsäss et al. Phys. Rev. B 65 (2002) 115410



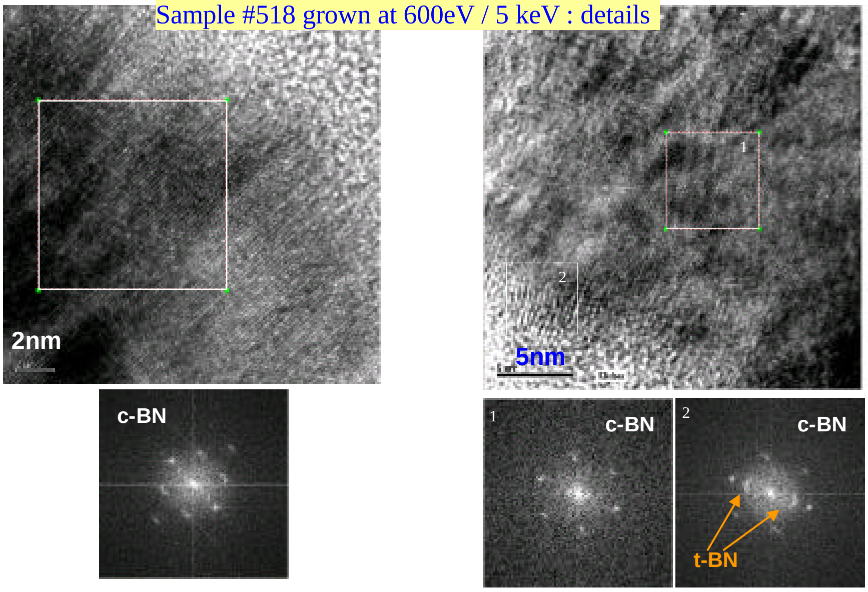
„Nucleation“ layer: T_S = 250 °C, E_{Ion} = 600 eV, Q = 0.2 C
„Growth“ layer: T_S = 250 °C, E_{Ion} = 3.5 and 5 keV, Q = 0.2 C



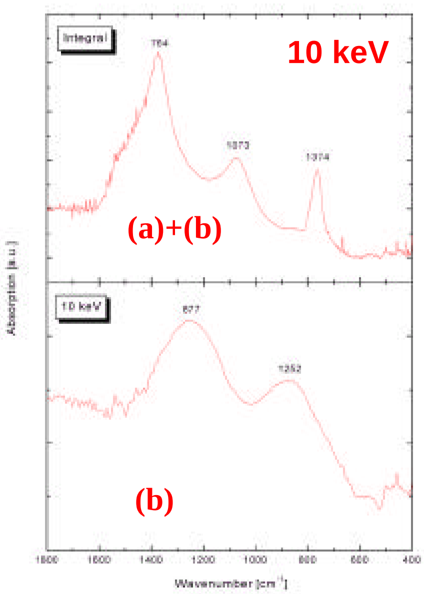
- high c-BN content (FTIR)
- sp^2-surface layer (EELS)
- c-BN growth possible at 5 keV

7 **High energy limit of c-BN growth:** **experiments with E_{Ion} ? 5 keV**

Sample #518 grown at 600eV / 5 keV : details



8 **High energy limit of c-BN growth:** **experiments with E_{Ion} =10 keV**



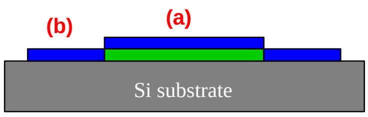
Sample #565 grown at 600eV / 10 keV

„Nucleation“ layer:

T_S = 250 °C, E_{Ion} = 600 eV, Q = 0.2 C

„Growth“ layer:

T_S = 250 °C, E_{Ion} = 10 keV, Q = 0.2 C



- only small fraction of c-BN (residual nucleation layer)
- E_{PL} < 26 eV

No c-BN growth

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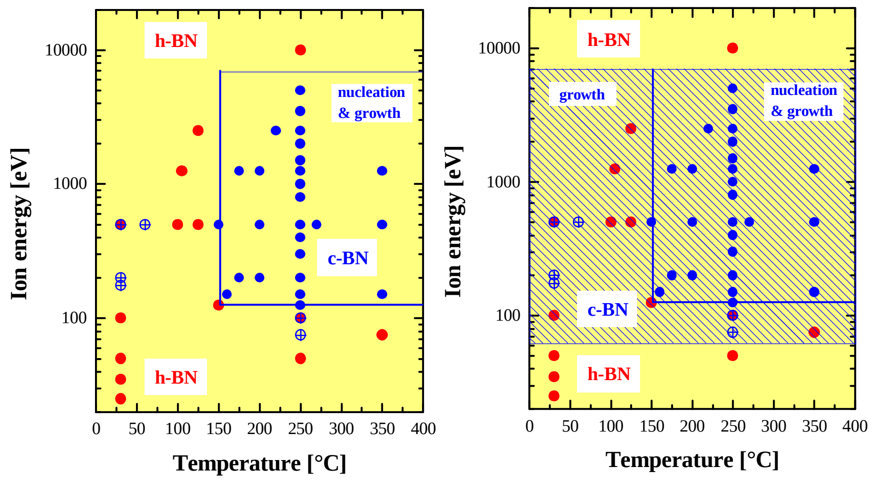
New BN phase formation diagram for MSIBD



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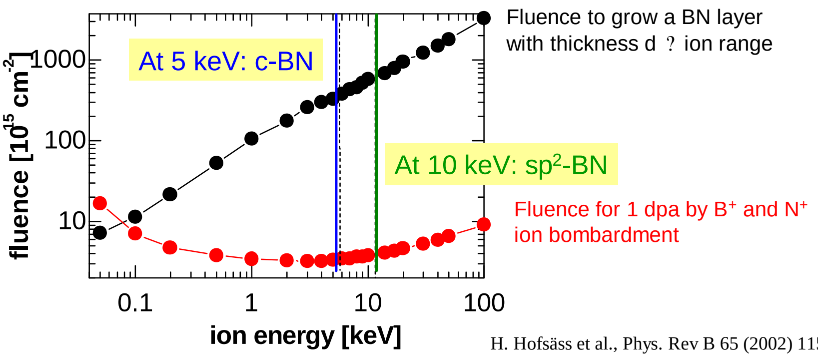
c-BN to sp²-BN transformation by ion irradiation

(1) P. Widmayer *et al.*, Diam. Relat. Mater. **6**, 216 (1997). 350 keV Kr
(2) J. Ullmann *et al.* , J. Appl. Phys. **83**, 2980 (1998). 1.1 MeV Xe
(3) C. Fitz *et al.*, Surf. Coat. Technol. **128-129**, 292 (2000). 35 keV Ar

c-BN to sp²-BN transformation at about 1 dpa accumulated damage



H. Hofsäss et al., Phys. Rev B 65 (2002) 115410

Accumulation of defects suppressed at 5 keV ! (due to thermal spikes ?)

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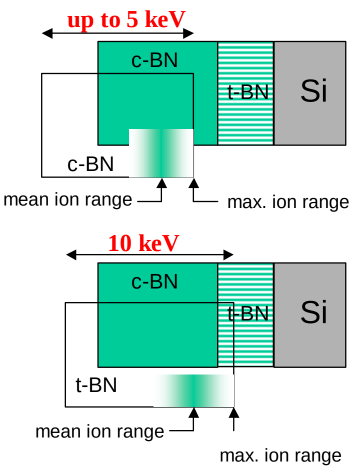
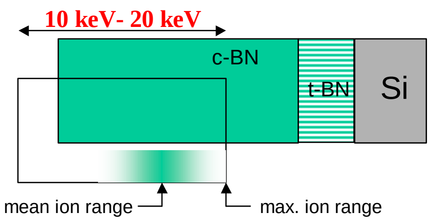
Recent BN growth and ion irradiation studies

Schematics of film growth

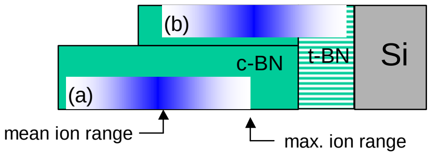
Previously studied films:



New set of BN films :



N^+, Ar^+ ion-irradiated BN films :
E_{ion}: 10 – 30 keV



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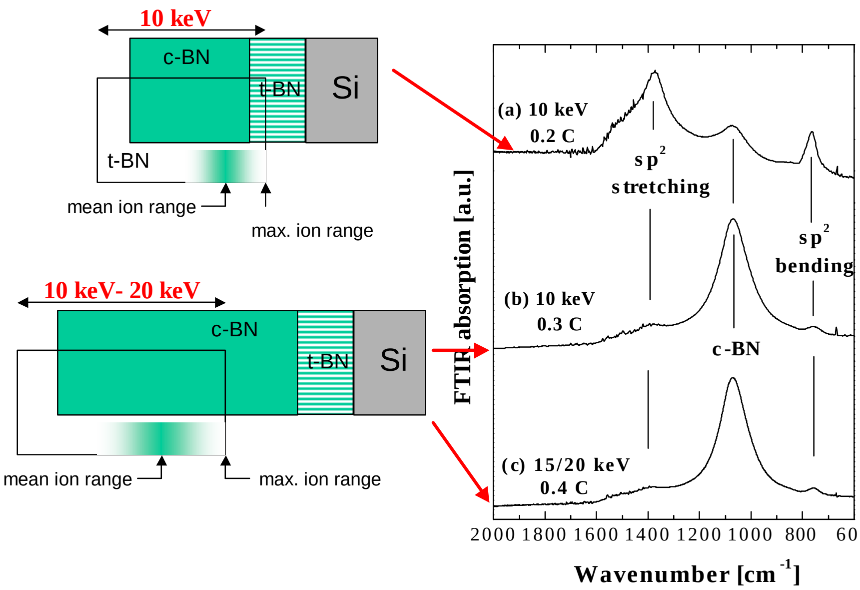
c-BN growth with up to 20 keV ions



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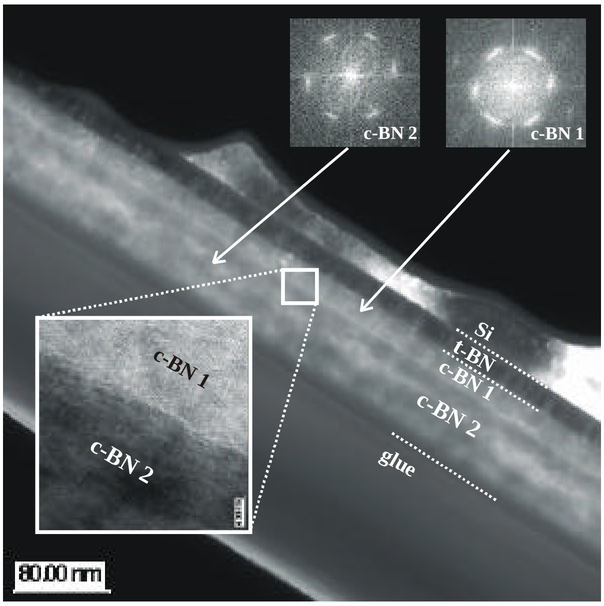
c-BN growth with up to 20 keV ions



Dark field TEM picture of a c-BN film (**c-BN 2**) grown with

10 keV B^+ ions and
13 keV N^+ ions

on previously grown c-BN film (**c-BN1**) using 600 eV ions

T_S = 250 °C

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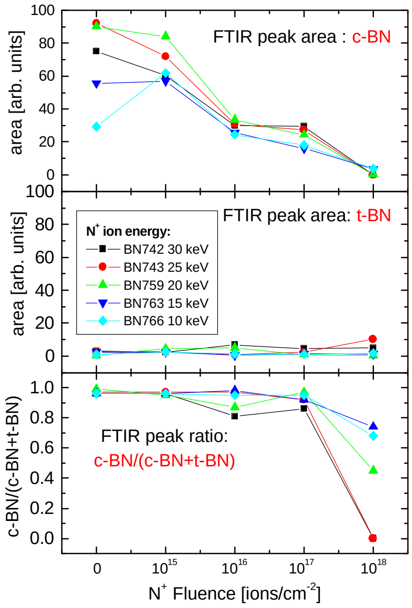
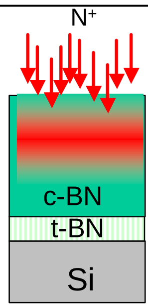
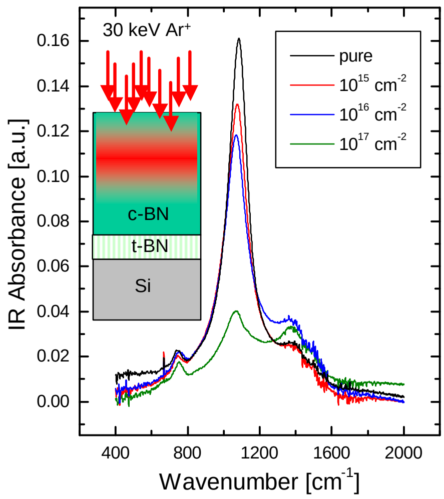
N^+ ion irradiation of c-BN films: 10 keV – 30 keV



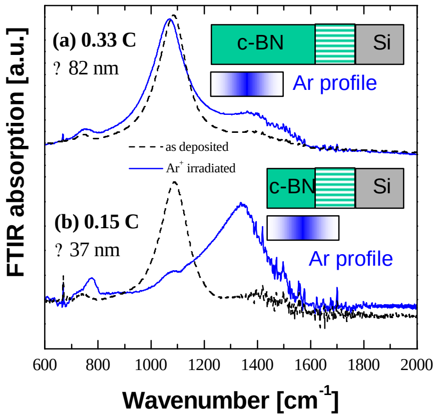


- high c-BN content up to 10^{17} N^+/cm^2 corresponding to about **25 dpa**
- significant reduction of c-BN absorption between 10^{15} and 10^{16} N^+/cm^{-2} (around **1 dpa**)

15 **Ar^+ ion irradiation of c-BN films: 10 keV - 30 keV**



30 keV Ar^+ ion irradiation
with fluence 10^{16} cm^{-2}



- high c-BN ✍ content up to 10^{16} Ar^+/cm^2 corresponding to about **10 dpa**
- ion irradiation reduces c-BN IR absorption

- c-BN/t-BN phase boundary instable to ion irradiation

16 **Summary**

- Low energy threshold for c-BN growth: 50 - 75 eV
- c-BN growth possible up to at least 20 keV ion energy !!!!
  What is the growth mechanism ?
- c-BN stable against N^+ ion irradiation up to 10^{17} cm^{-2} (? **25 dpa**)
- c-BN stable against Ar^+ ion irradiation up to 10^{16} - 10^{17} cm^{-2} (? **10 dpa**)
- c-BN/t-BN interface instable under ion irradiation !!! (? **1 dpa**)
- strongly reduced c-BN IR-absorption due to ion irradiation (? **1 dpa**)
  - TEM still shows c-BN !
  What determines the c-BN IR absorption intensity ?