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INSTITUUT VOOR MATERIAALONDERZOEK

FABRICATION AND PROPERTIES OF NANOCRYSTALLINE DIAMOND FILMS

Dr. Stoffel D. Janssens and Prof. Dr. K. Haenen

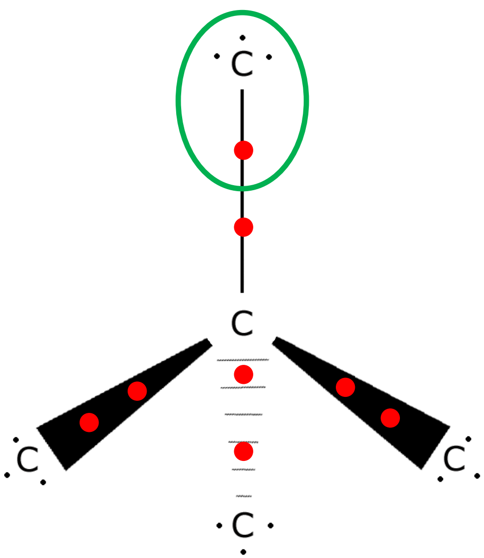
Outline

- Diamond
- Diamond growth
- Intrinsic NCD layers
- Boron-doped NCD

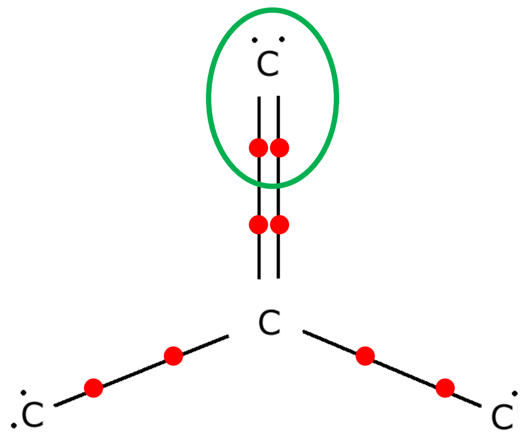
Diamond

- Carbon atoms
  → 4X attached to each other

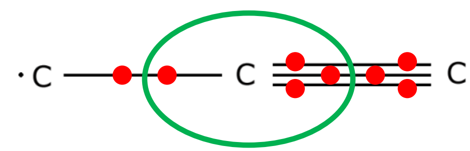
4 electrons per carbon atom



SP^3

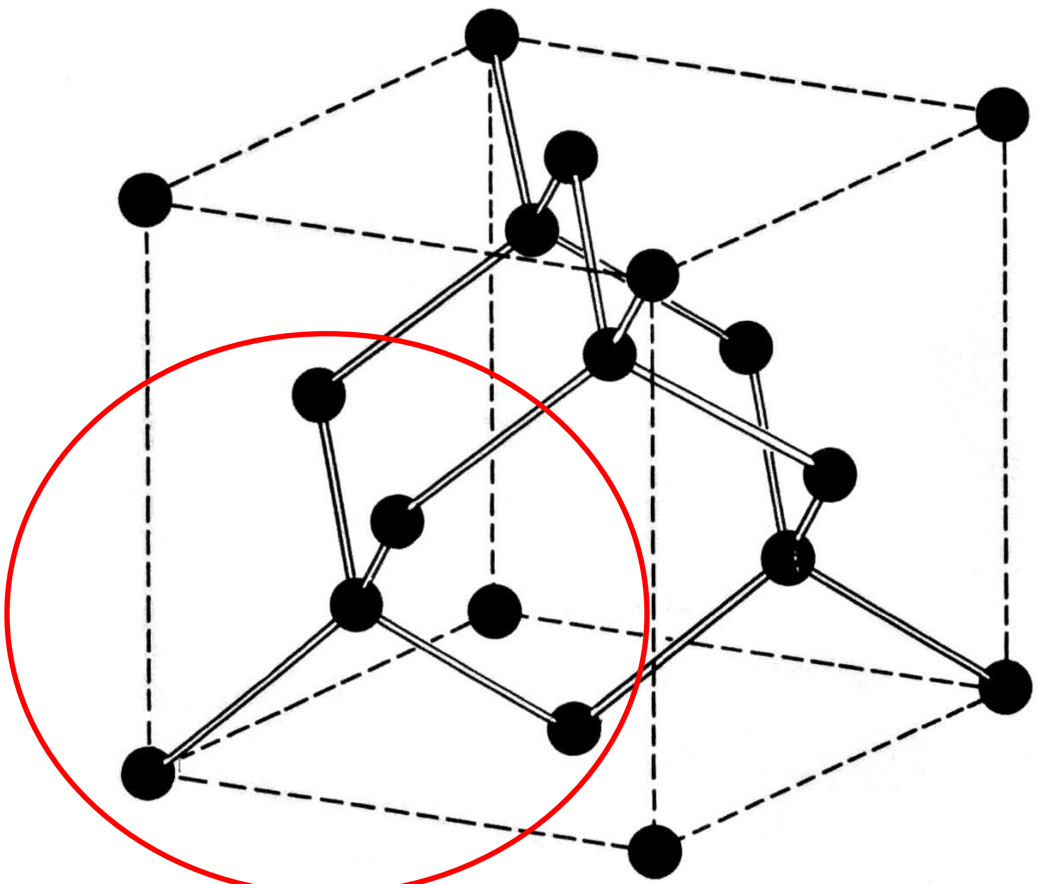


SP^2



SP

Diamond



- Carbon → 4 bonds
- Crystal
- Cubic crystal lattice

Introduction to Solid State Physics (C. Kittel)

Diamond: properties

Chemical

- Resistant to chemical corrosion
  (survives strong acidic treatments)
- Biologically compatible
  (no rejection by human body)
- Radiation hard
  (survives heavy radiation)
- High electrochemical window

Diamond: properties

Optical / Thermal

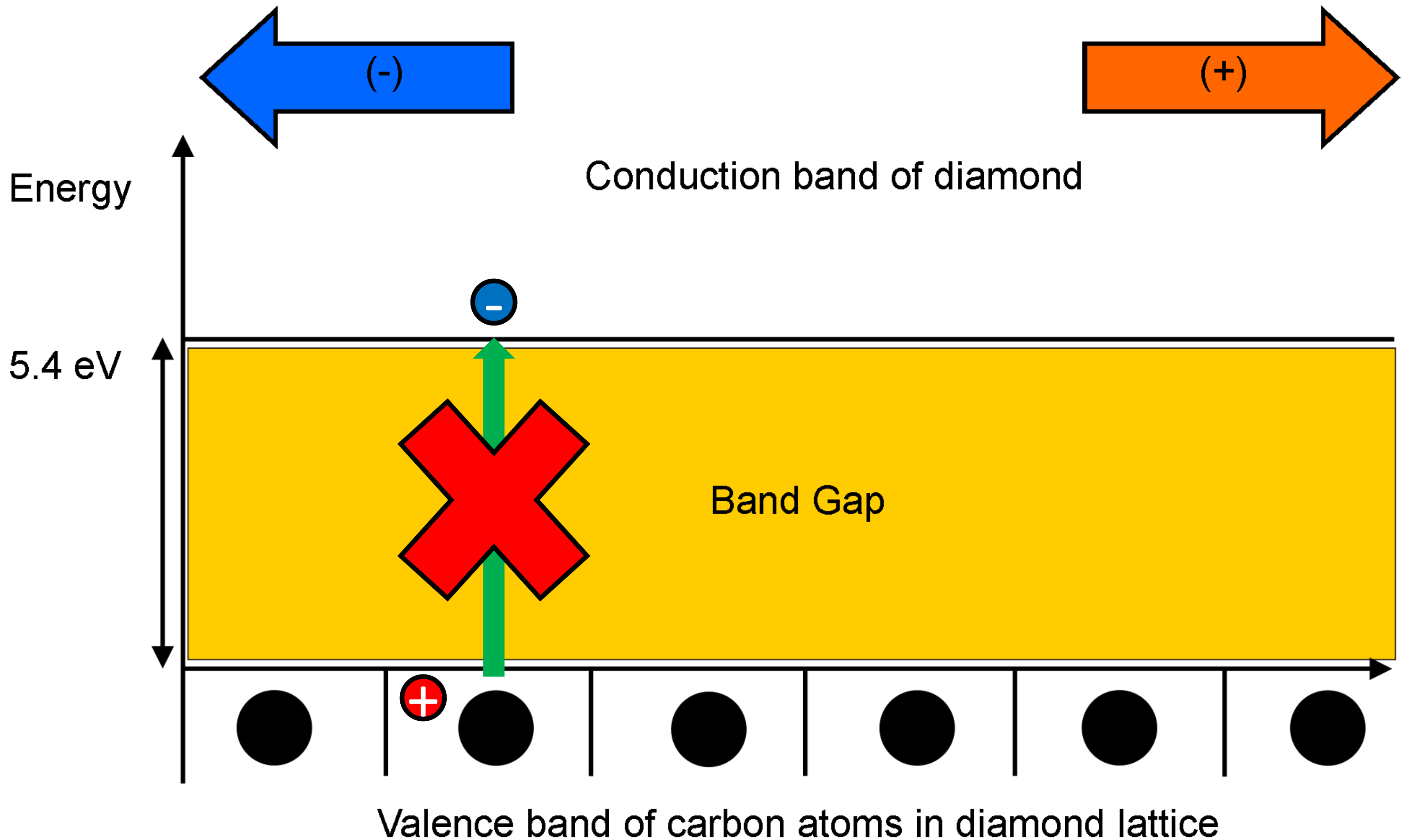
- Broad optical transparency from UV to IR
  (Sun tanning behind a diamond window)
- High thermal conductivity
  (Fast heat energy transport)
- Low thermal expansion coefficient
  (Not shrinking much, when cooling down)

Diamond: properties

Electronic / Mechanical

- High electrical resistivity
  (Difficult to create charge carriers)

High electrical resistivity

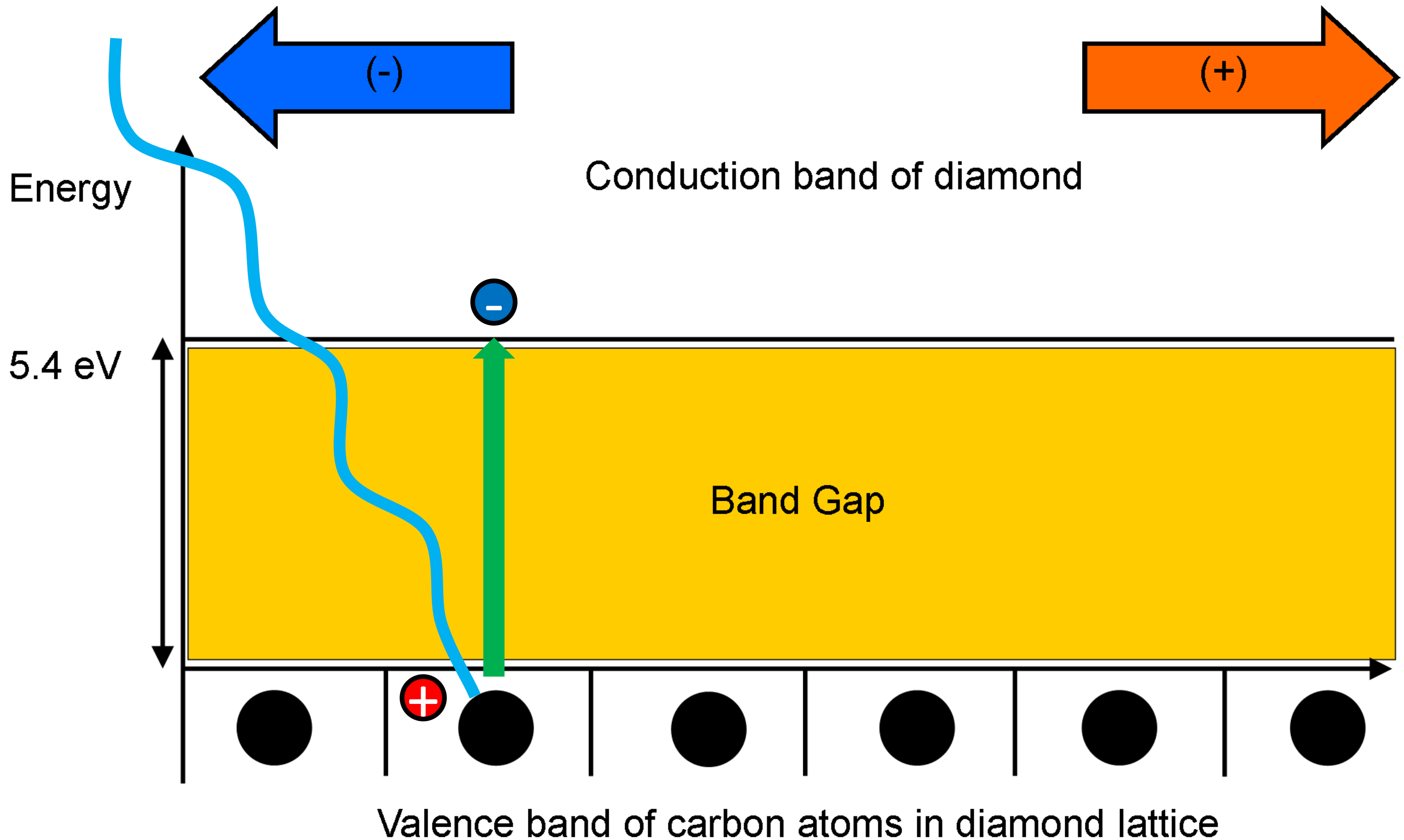


Diamond: properties

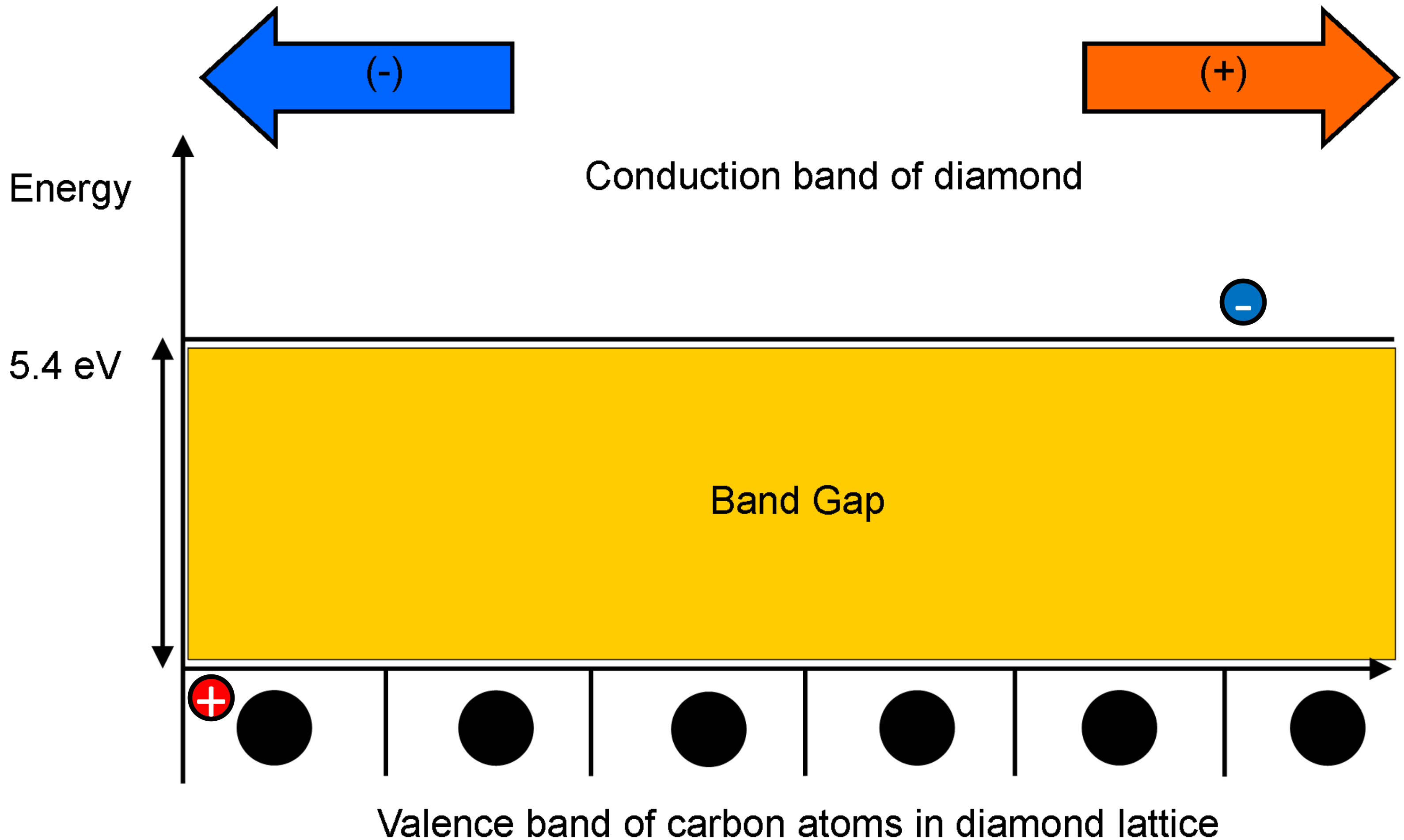
Electronic / Mechanical

- High electrical resistivity
  (Difficult create charge carriers)
- <u>High electrical mobility</u>
  <u>*(Once charge carriers are created, they are easily transported)*</u>

High electrical mobility



High electrical mobility



Diamond: properties

Electronic / Mechanical

- High electrical resistivity
  (Difficult create charge carriers)
- High electrical mobility
  (Once charge carriers created, they are easily transported)
- Hardest material
  (It scratches everything)

Diamond: doped

Boron: $3\ e^-$

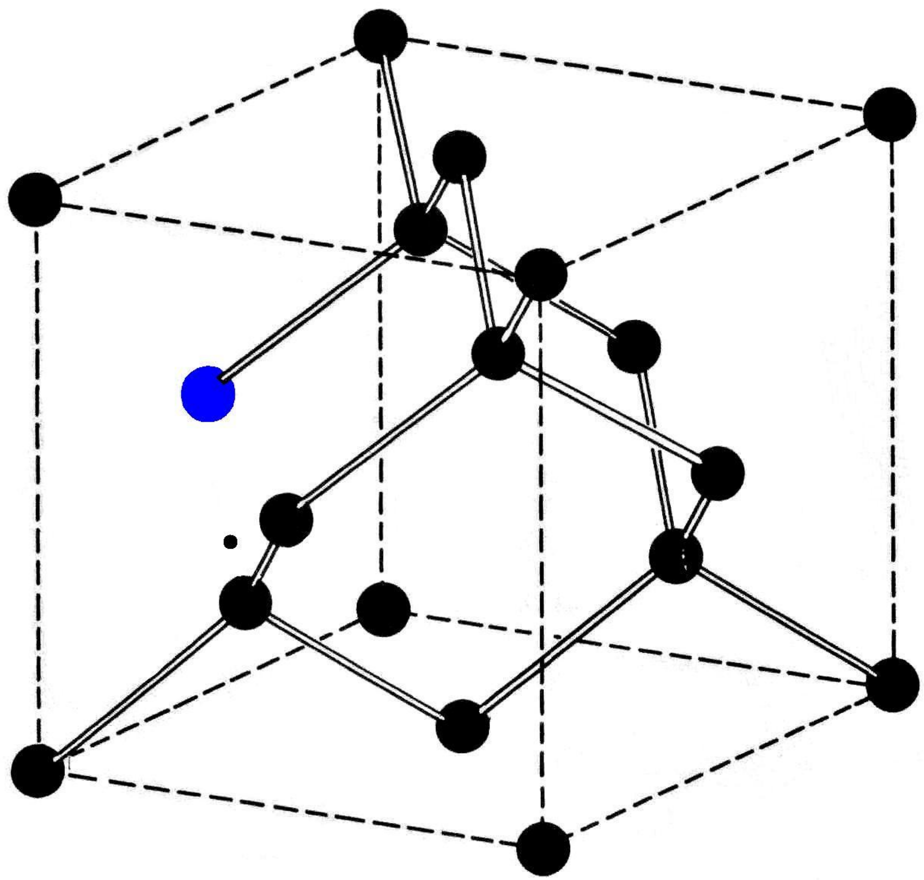
Carbon: $4\ e^-$

Nitrogen: $5\ e^-$

Phosphorus: $5\ e^-$

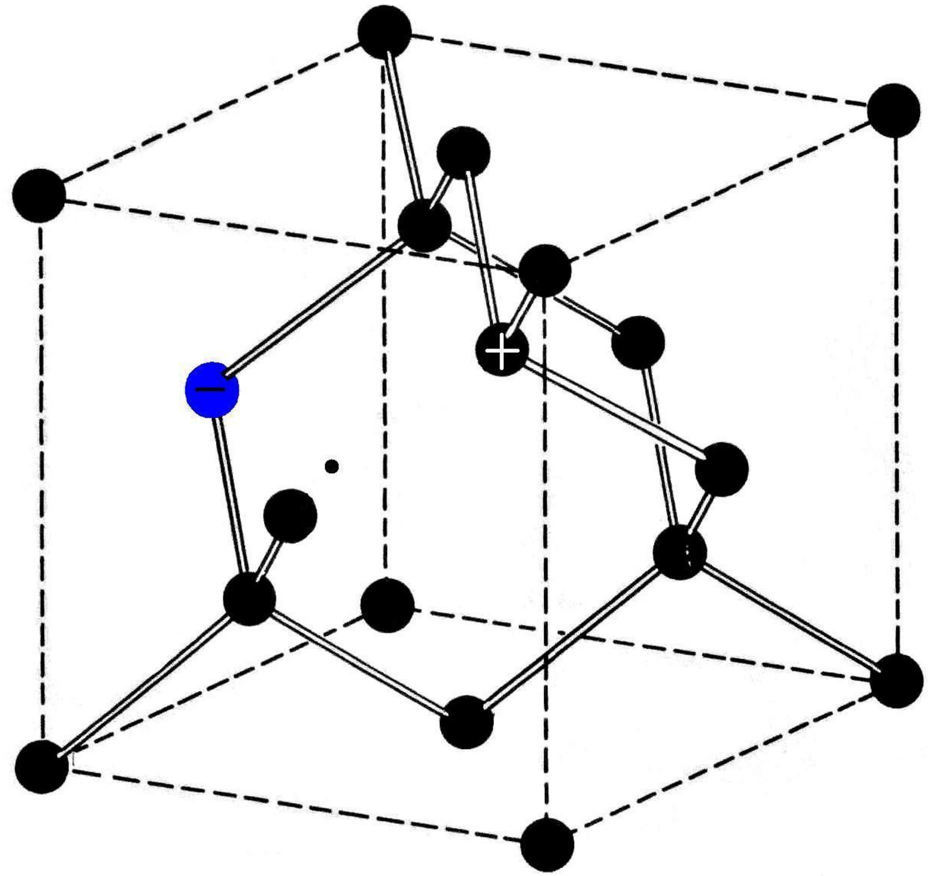
Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIIIb	VIIIb	VIIIb	Ib	IIb	IIIa	IVa	Va	VIa	VIIa	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	(43) Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	**	(104) Rf	(105) Db	(106) Sg	(107) Bh	(108) Hs	(109) Mt	(110) Ds	(111) Rg	(112) Cn	(113) Uut	(114) Uuq	(115) Uup	(116) Uuh	(117) Uus	(118) Uuo
		57 La	58 Ce	59 Pr	60 Nd	(61) Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		89 Ac	90 Th	91 Pa	92 U	(93) Np	(94) Pu	(95) Am	(96) Cm	(97) Bk	(98) Cf	(99) Es	(100) Fm	(101) Md	(102) No	(103) Lr	

Diamond: doped (Boron)



- Boron-doped diamond
- B binds 1 time less
- One bond → 2 electrons
- T = 0 K

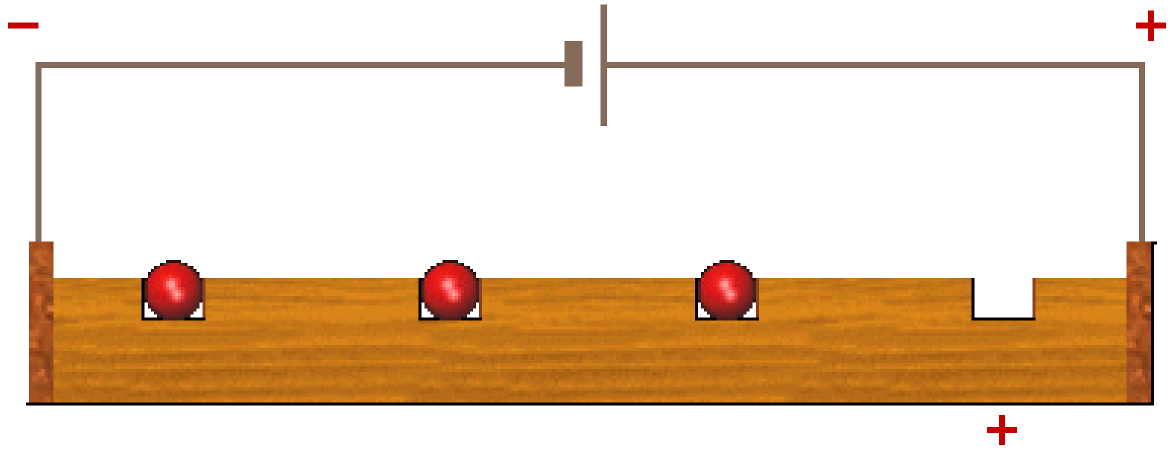
Diamond: doped (Boron)



- T = 0 K → T > 0 K
- Hole floats around
- P-type semiconductor (holes are Positive and float around)

Diamond: doped (Boron)

- Hole conduction!!!

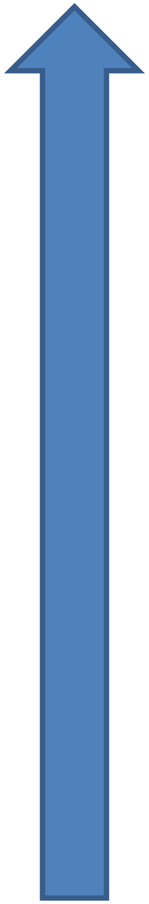


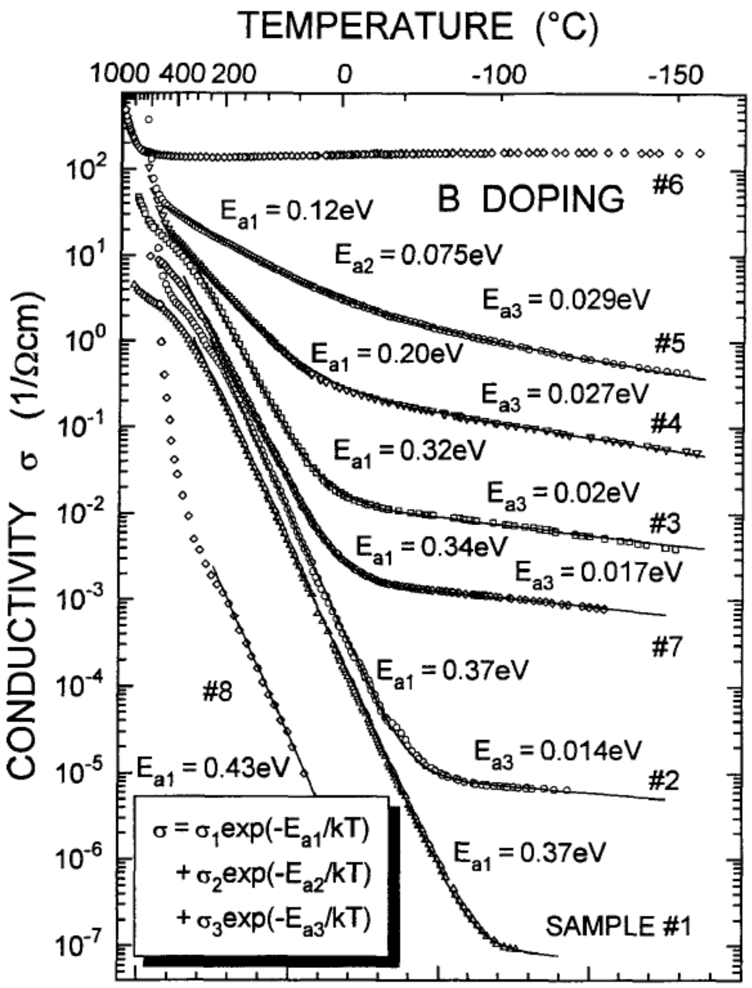
Diamond: doped (Boron)

- What are the effects of boron incorporation?
- Improvement of some properties

  <u>*-(Higher conductivity)*</u>

Higher conductivity





Borst et al., Diamond Relat. Mater. **4**, 948 (1995).

Diamond: doped (Boron)

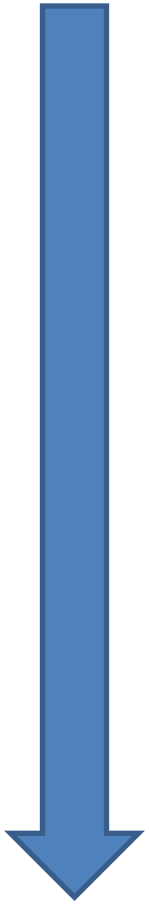
- What are the effects of boron incorporation?
- Improvement of some properties

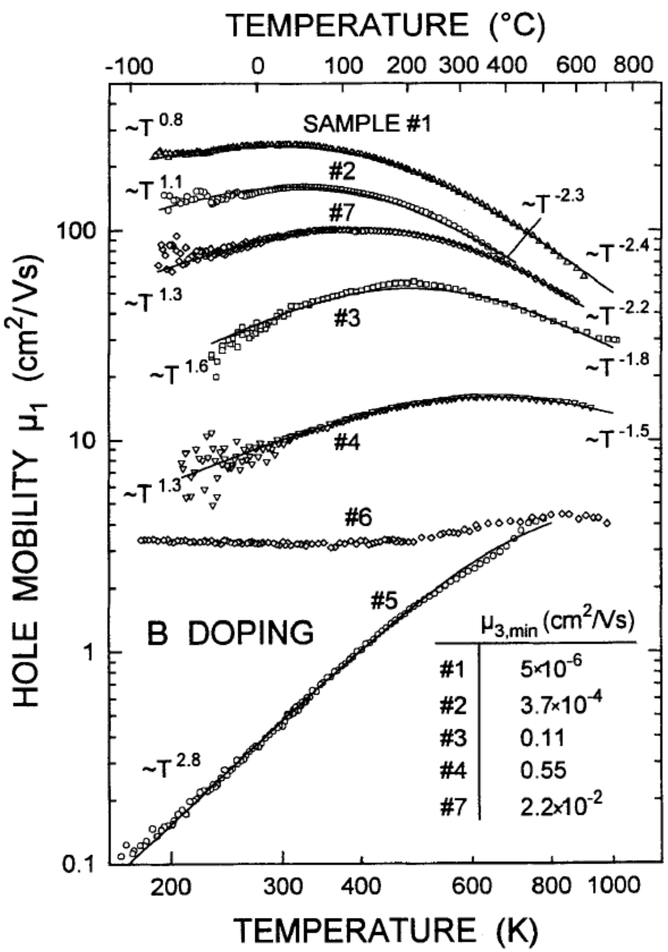
  -*(Higher conductivity)*

  but losses for other properties

  -*(Lower hole mobility)*

Lower hole mobility





Borst et al., Diamond Relat. Mater. **4**, 948 (1995).

Diamond: doped (Boron)

- What are the effects of boron incorporation?
- Improvement of some properties

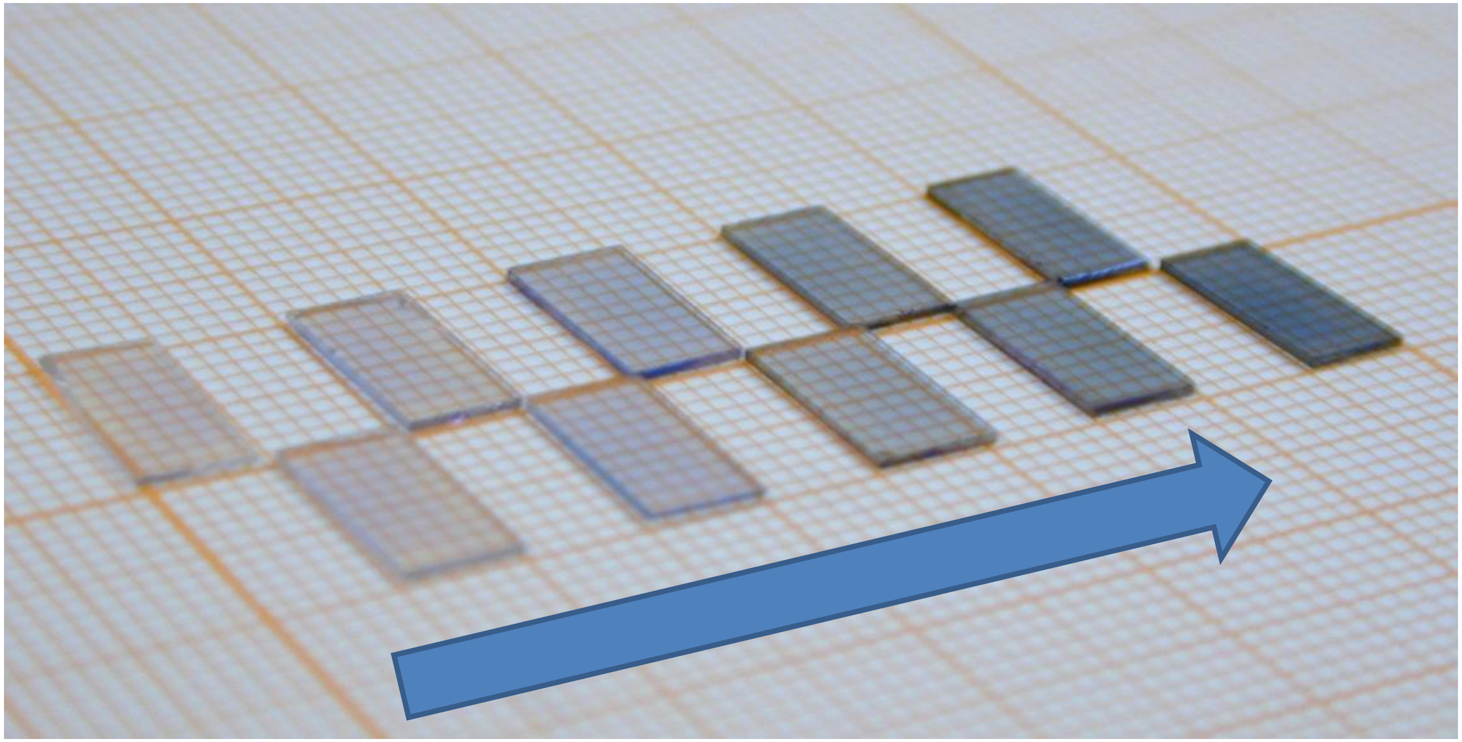
  -*(Higher conductivity)*

  but losses for other properties

  -*(Lower hole mobility)*

  -*(Lower optical transparency)*

Lower optical transparency

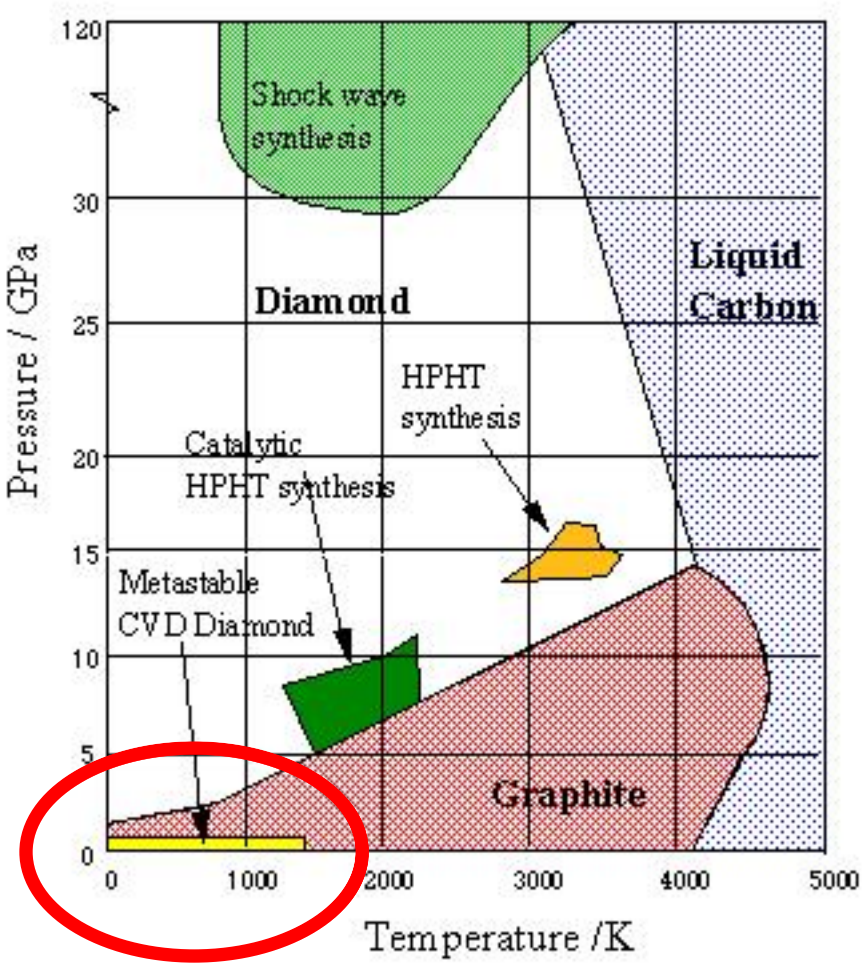


Outline

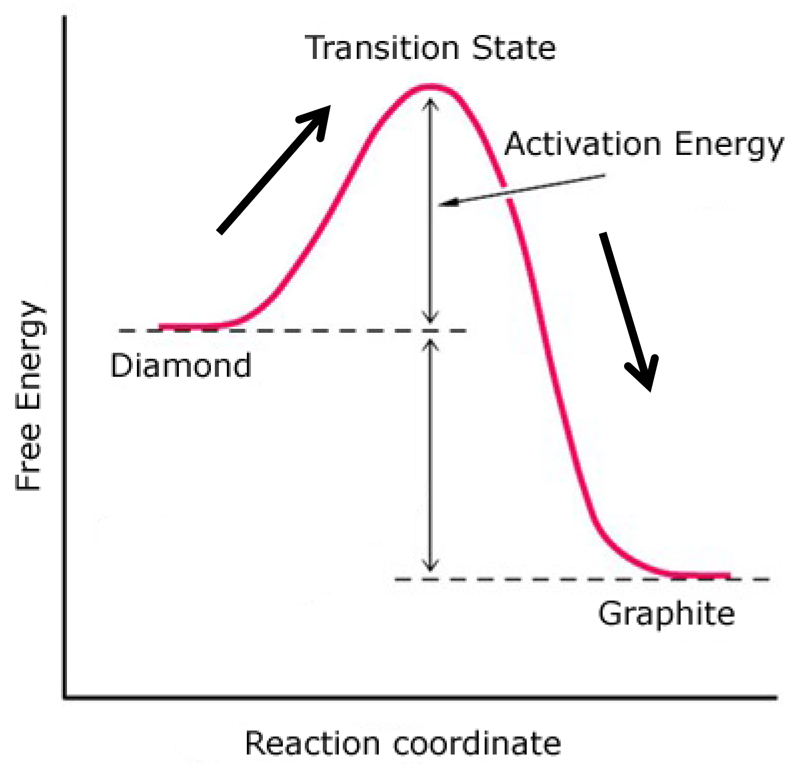
- Diamond
- Diamond growth
- Intrinsic NCD layers
- Boron-doped NCD

Diamond growth

- Bundy et al.
  Phase diagram of carbon

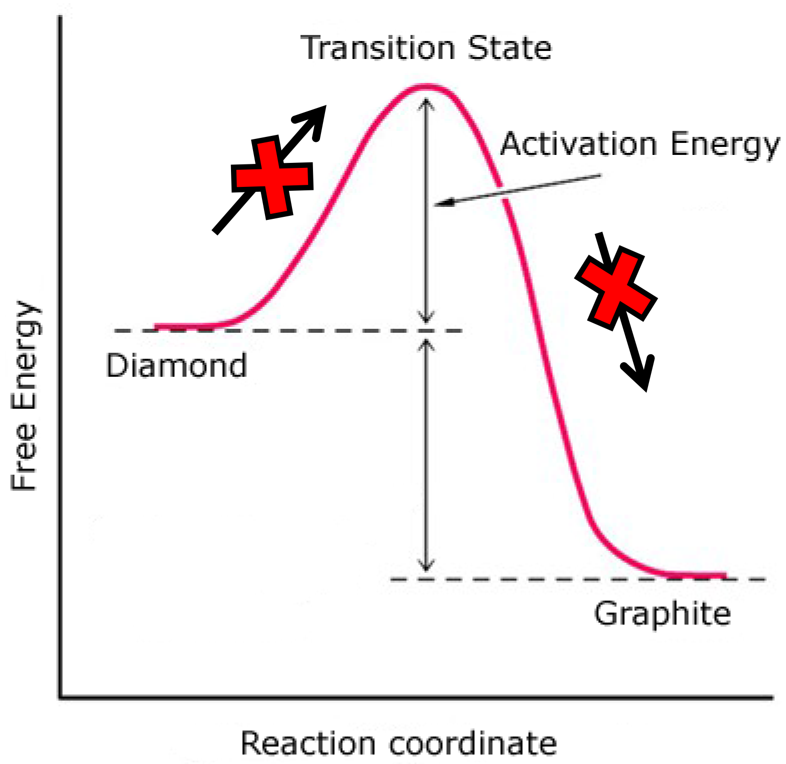


Diamond growth: Energy diagram



- Easily over barrier
  → Diamond unstable

Diamond growth: Energy diagram

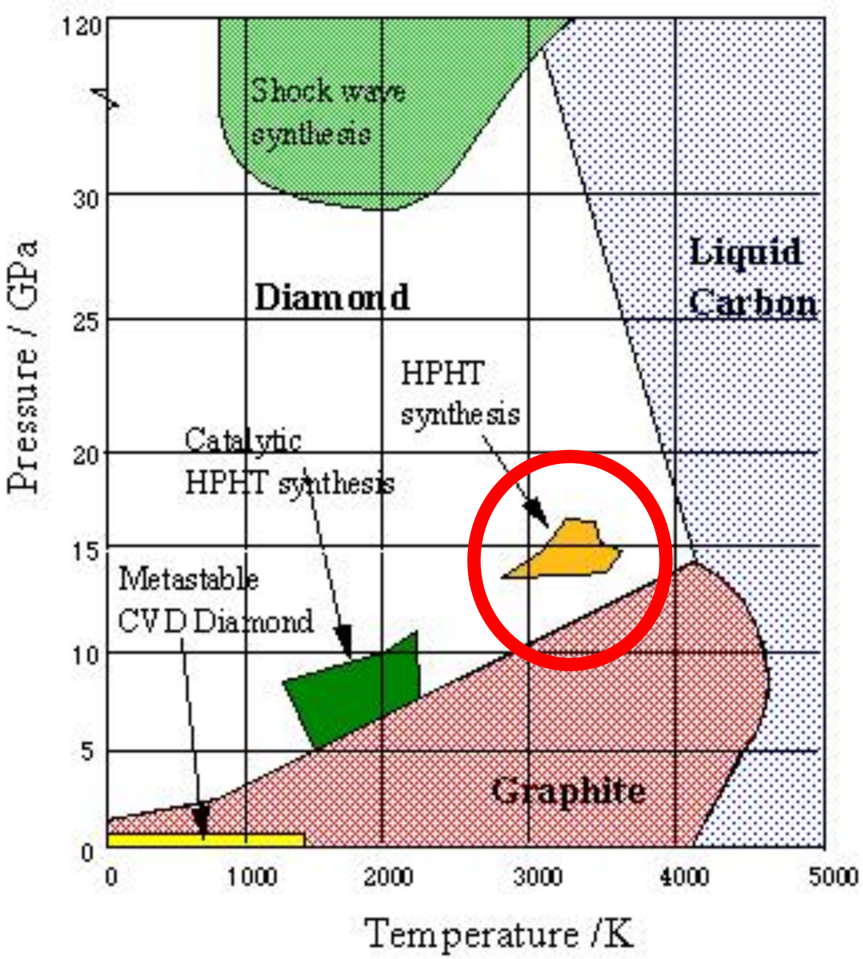


- Easily over barrier
  → Diamond unstable
- Very difficult over barrier
  → Diamond metastable

Last scenario at standard ambient conditions.

Diamond growth: HPHT (Nature)

- Bundy et al.
  Phase diagram of carbon
- HPHT
  -Nature's way (till 4 cm diameter)



Diamond growth: HPHT (Nature)

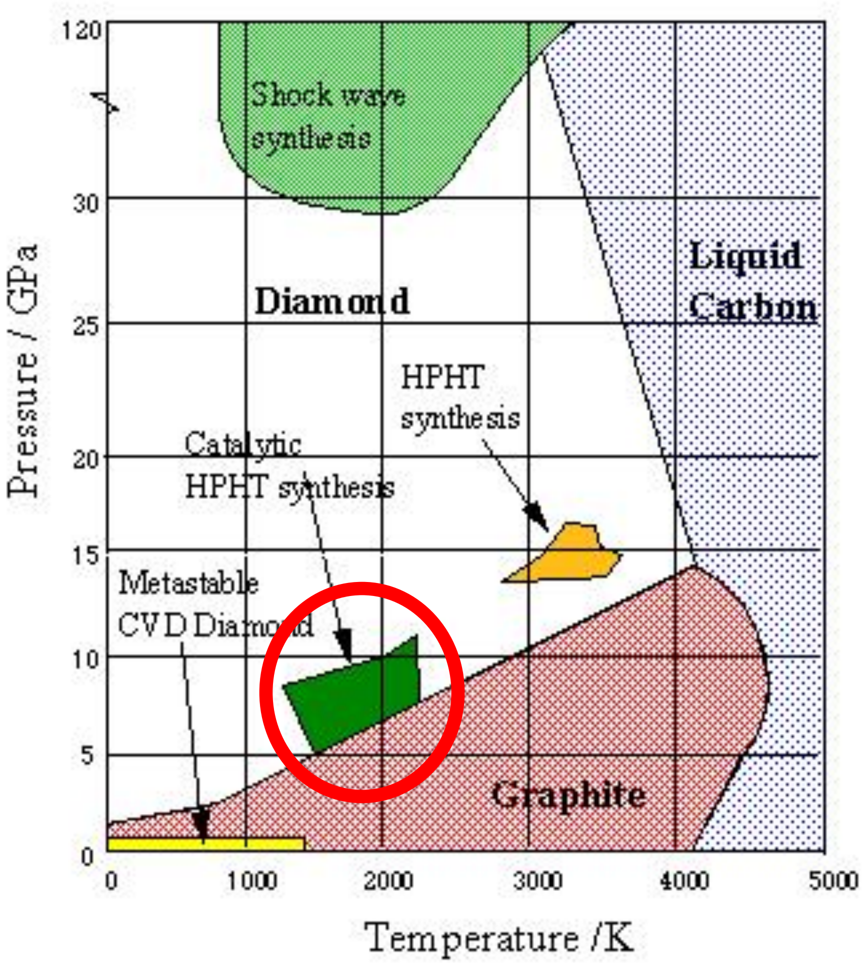
Size:
Approximately 12.4 x 10.5 x 8.4 mm
Location:
natural diamond rough mined in Congo
Price:
$547.20

This natural diamond crystal weighs 6.84 carats! It is translucent to semi-transparent with a cubic shape. Its in very good condition overall, and it has greyish-yellowish-green natural color.

http://www.mineralminers.com/html/diamins.stm

Diamond growth: HPHT (Synthetic)

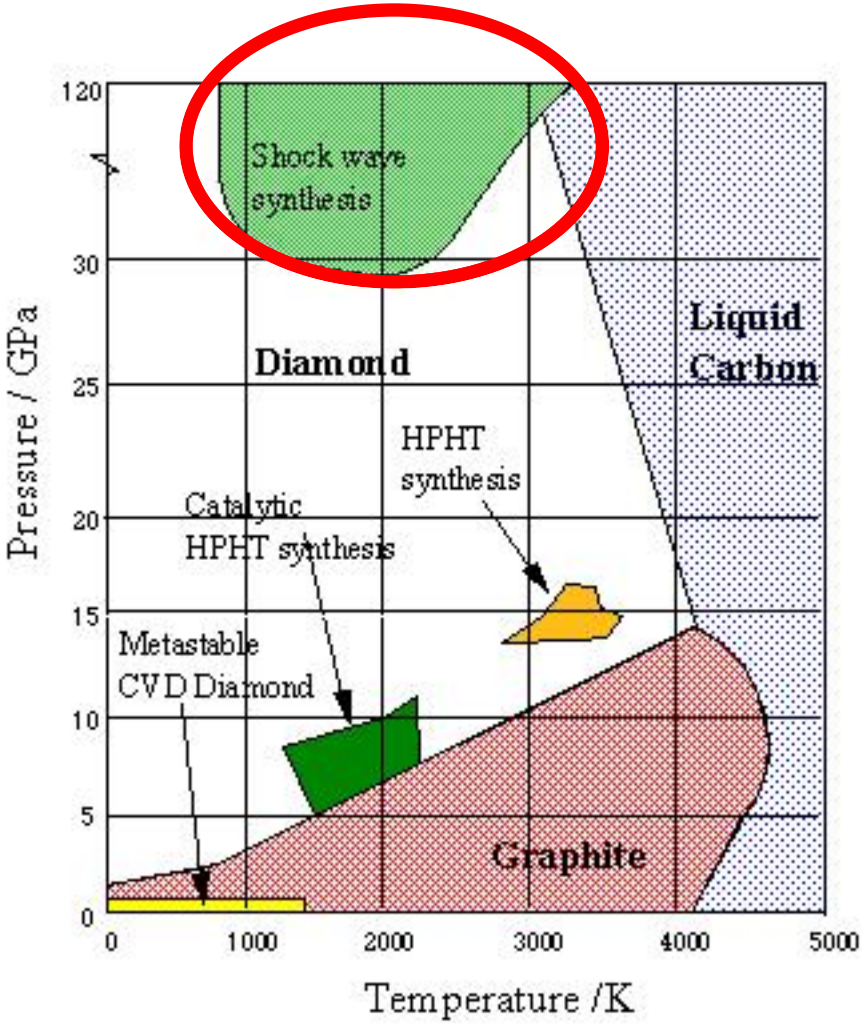
- Bundy et al.
  Phase diagram of carbon
- HPHT
  -Natures way
  (till 4 cm diameter)
  -<u>Synthetic (Catalytic)</u>
  <u>(Large diamonds (mm))</u>



Diamond growth: HPHT (Synthetic)

Diamond growth: Shock wave

- Bundy et al.
  Phase diagram of carbon
- <u>Shock wave:</u>
  <u>*TNT in vessel*</u>
  <u>*(5 to 10 nm diameter)*</u>



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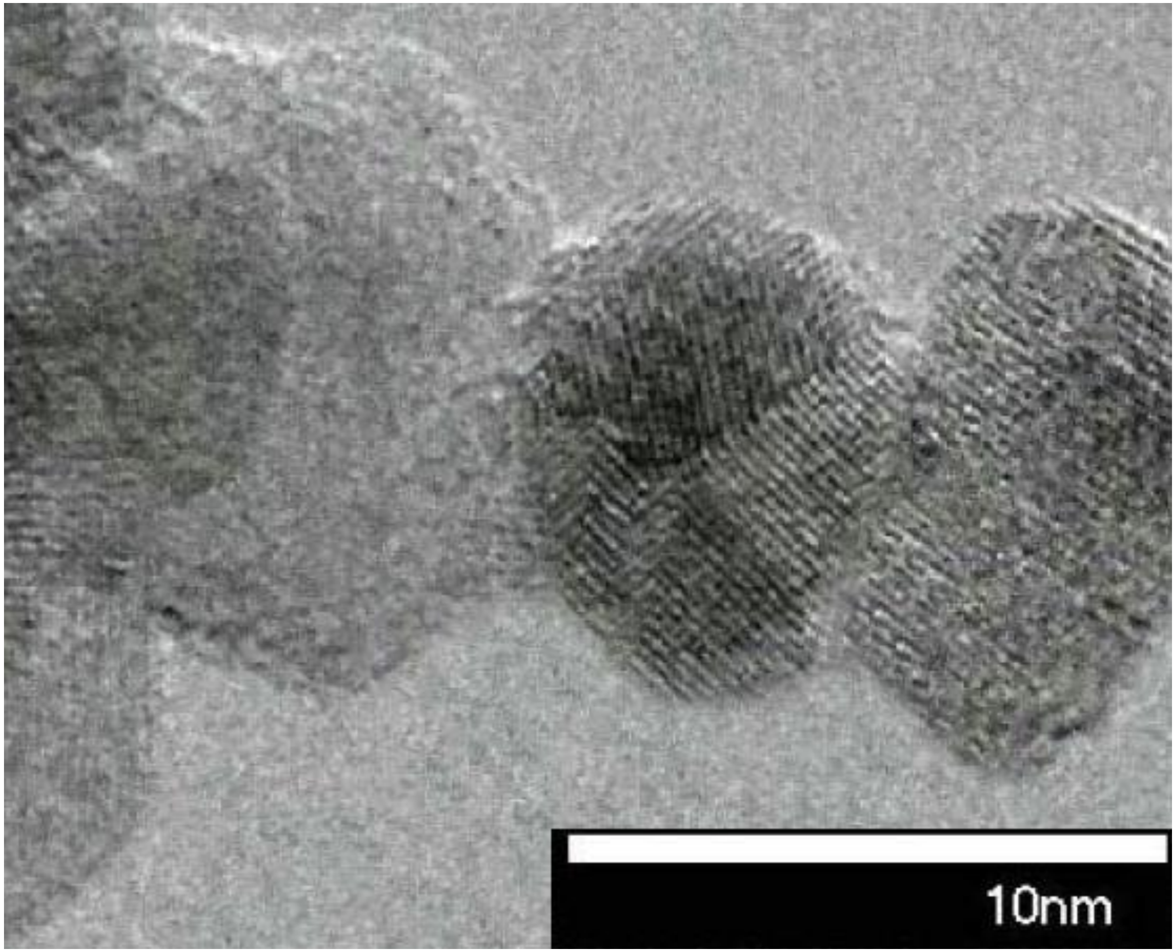
Diamond growth: Shock wave



Iakoubovskii et al., Nanotechnology **19**, 155705 (2008)

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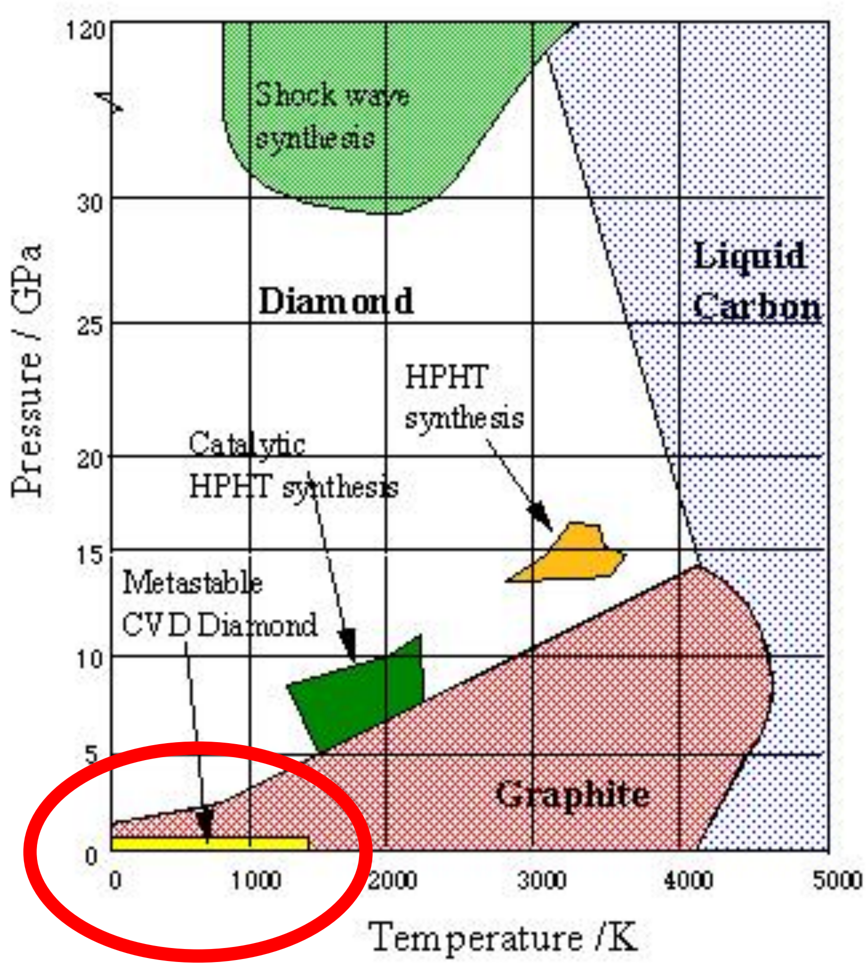
Diamond growth: CVD

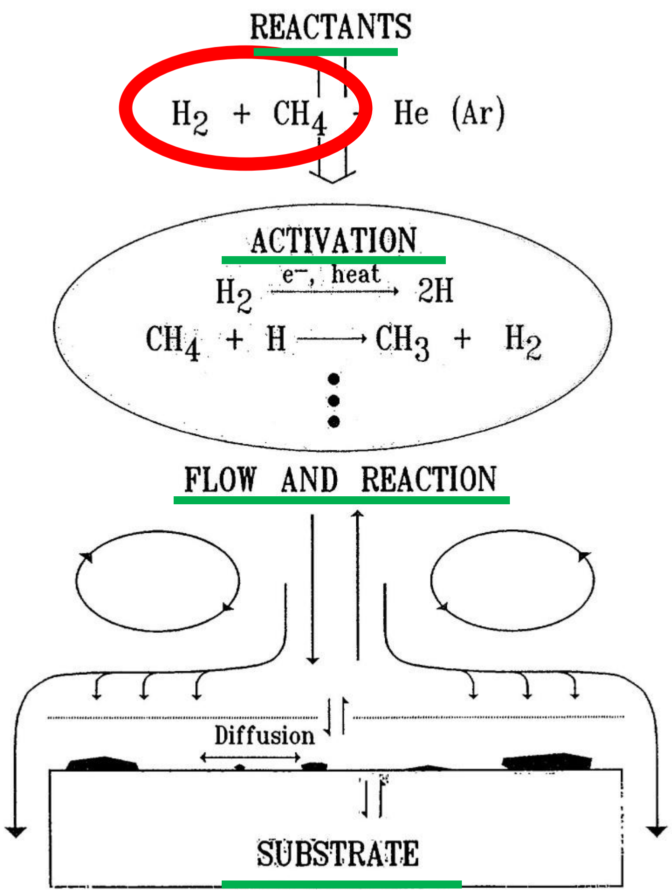
- Bundy et al.
  Phase diagram of carbon
- <u>Chemical vapor deposition (CVD)</u>
  <u>-Highly pure diamond</u>
  <u>-P,N,B-doping</u>
  <u>-Thin or thick layers</u>
  <u>-Polycrystalline diamond</u>

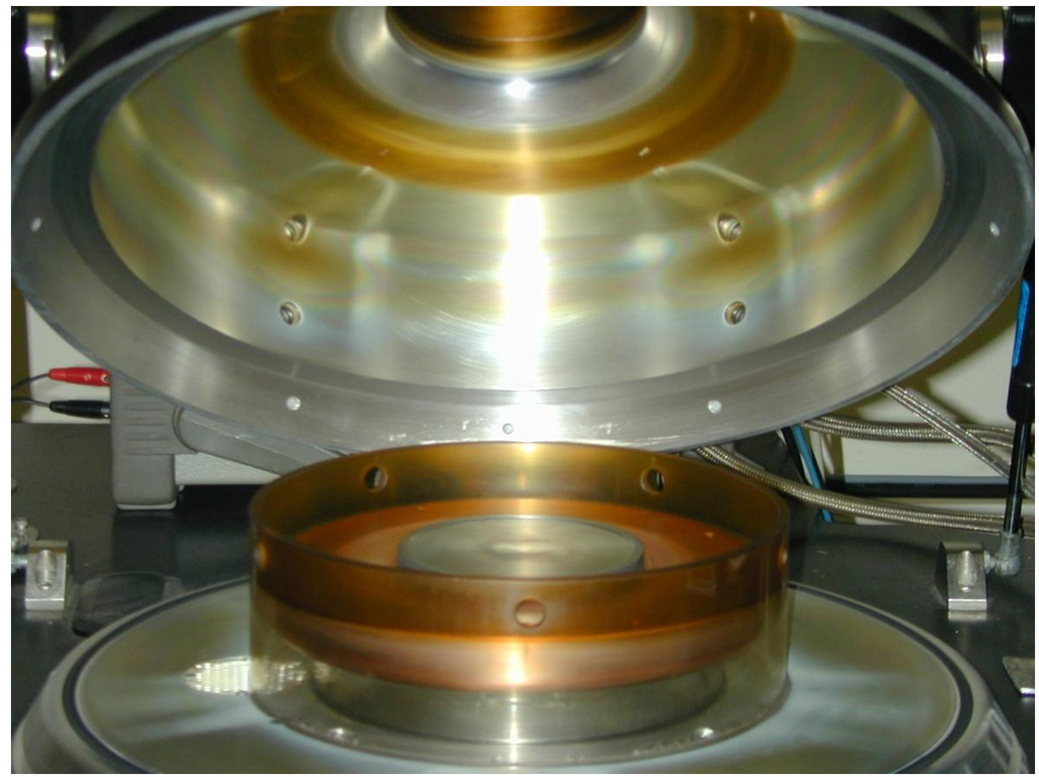


Diamond growth: CVD

ASTeX 6500

Diamond growth: CVD



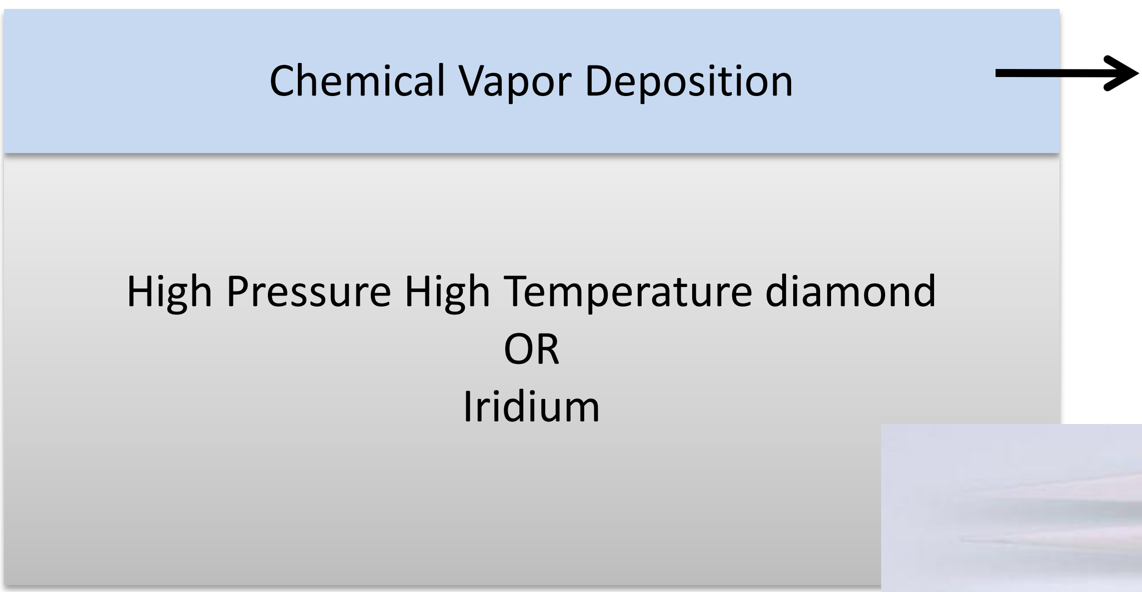


- ➢Carbon/Hydrogen-ratio (C/H-ratio): low
- ➢Doping (TMB, PH_3, N_2)

Butler et al. Phil. Trans. R. Soc. A **342**, 209 (1993)

Diamond growth: CVD (Substrates)

Single crystal diamond



- Pure (intrinsic)
- Boron-doped
- Phosphorus-doped
- Nitrogen-doped

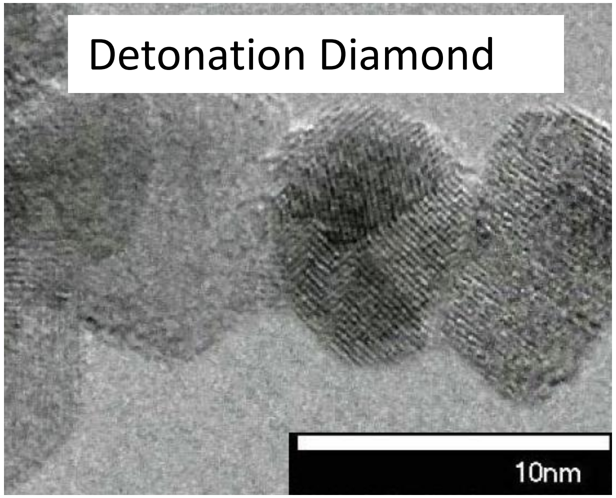
...

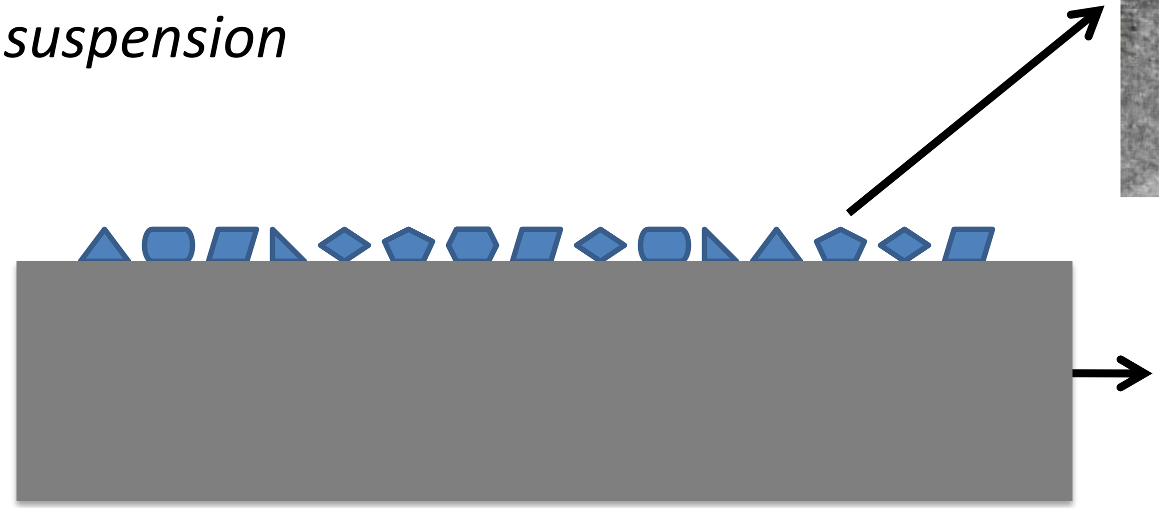
http://www.e6.com/

Diamond growth: CVD (Substrates)

Polycrystalline diamond

Dipping of substrate in detonation diamond suspension

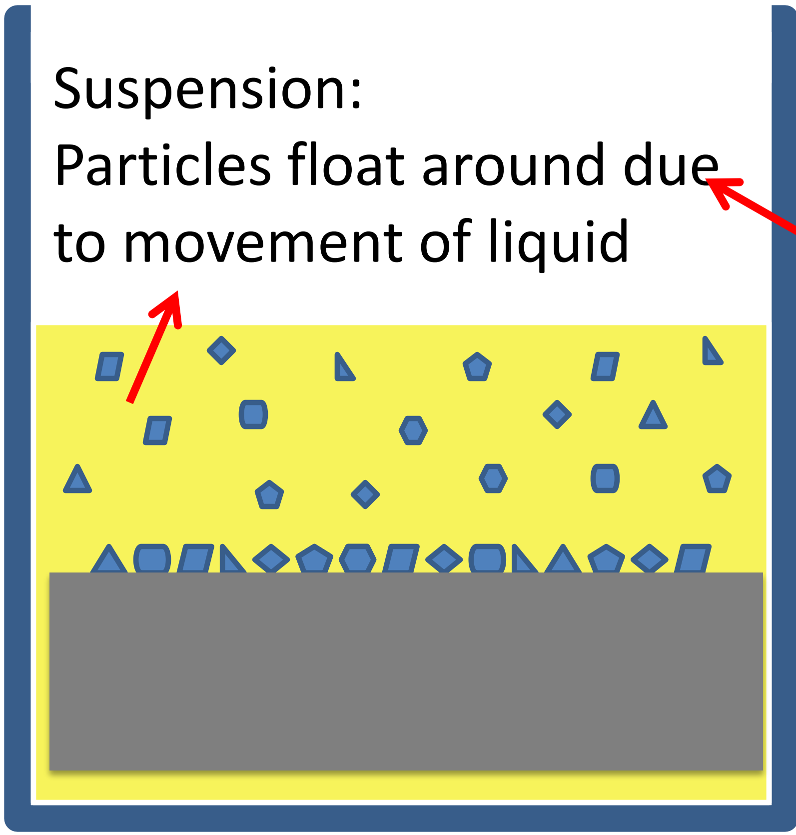


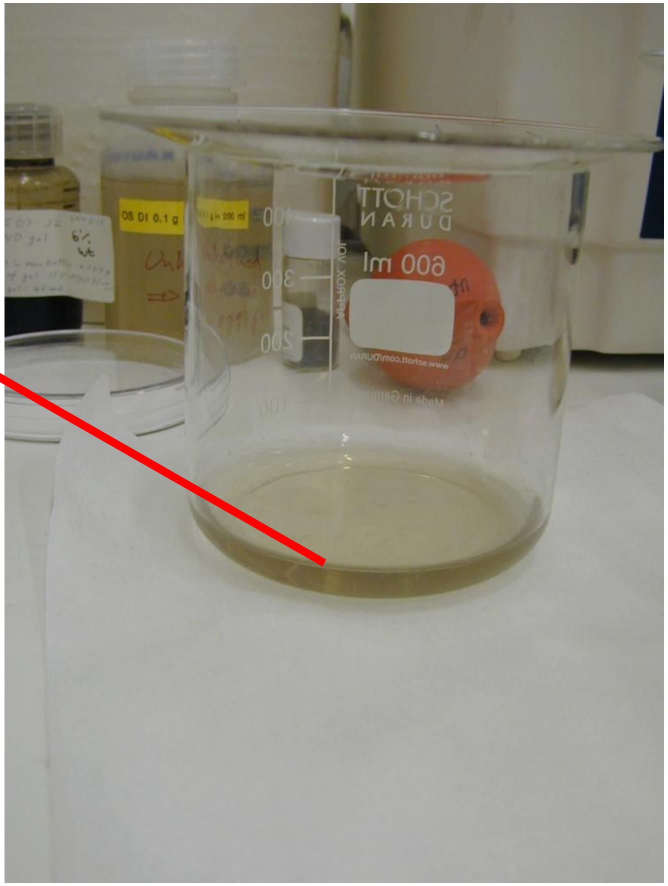


Silicon, Pure glass (fused silica), Tungsten, ...

Diamond growth: CVD (Substrates)

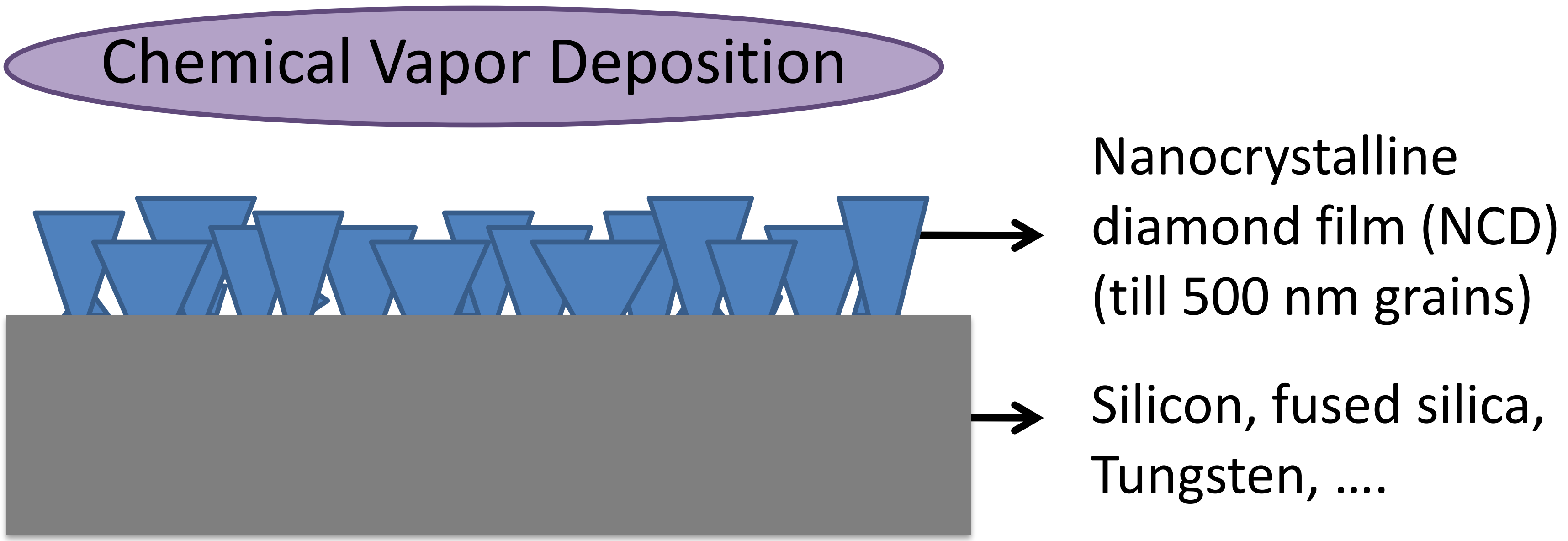
Polycrystalline diamond





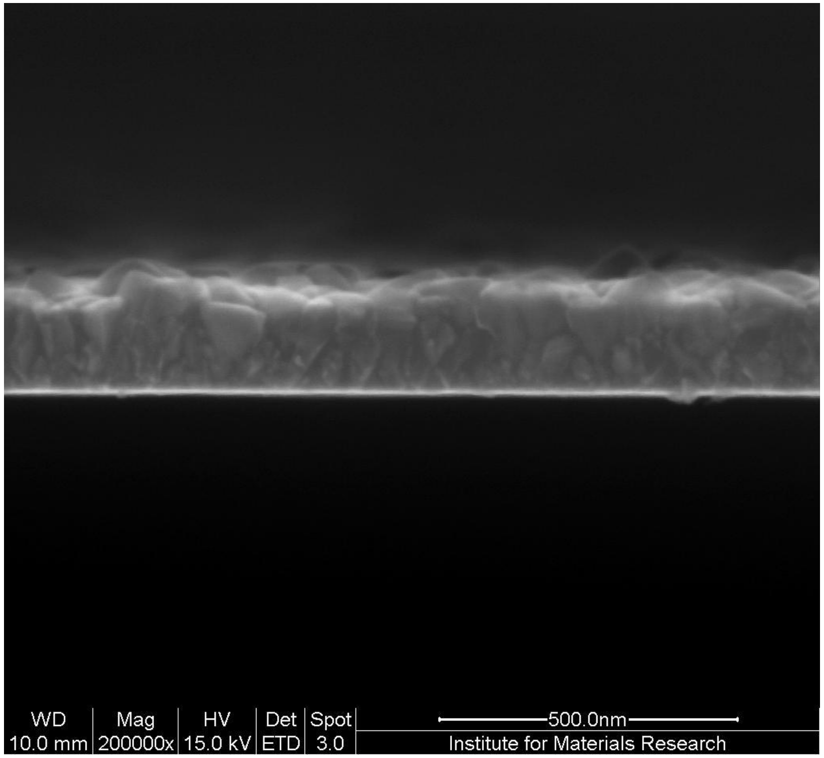
Diamond growth: CVD (growth)

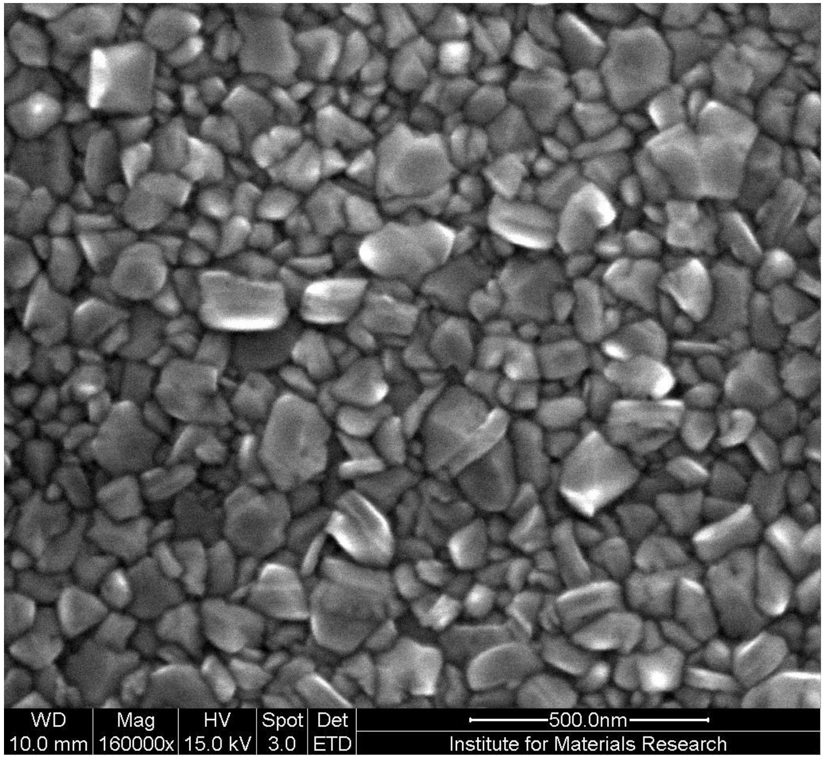
Polycrystalline diamond: *nanocrystalline diamond*



Diamond growth: Characterization

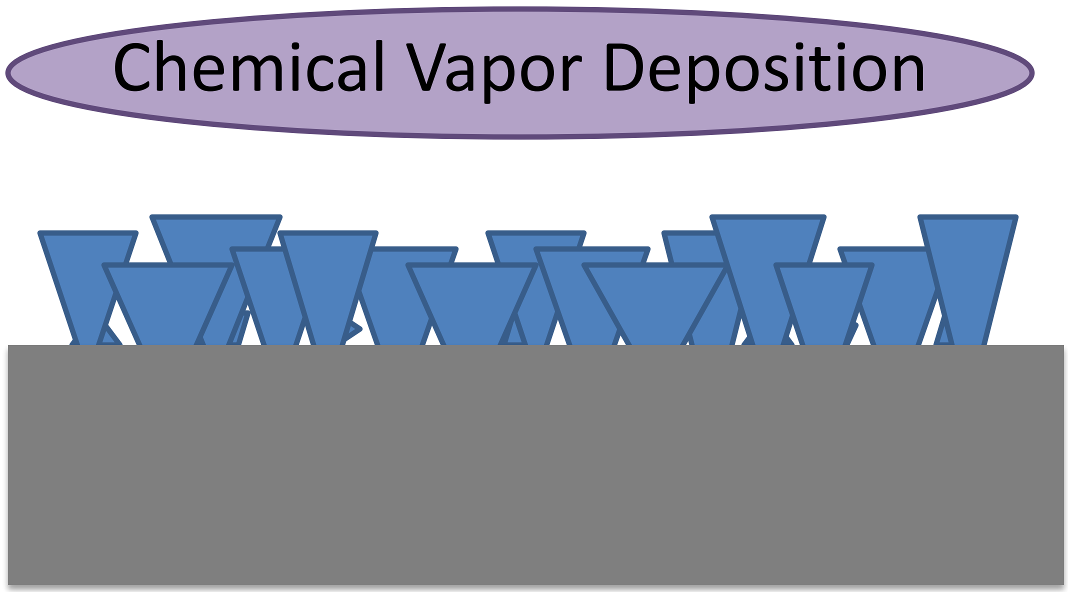
Scanning electron microscopy: *nanocrystalline diamond*





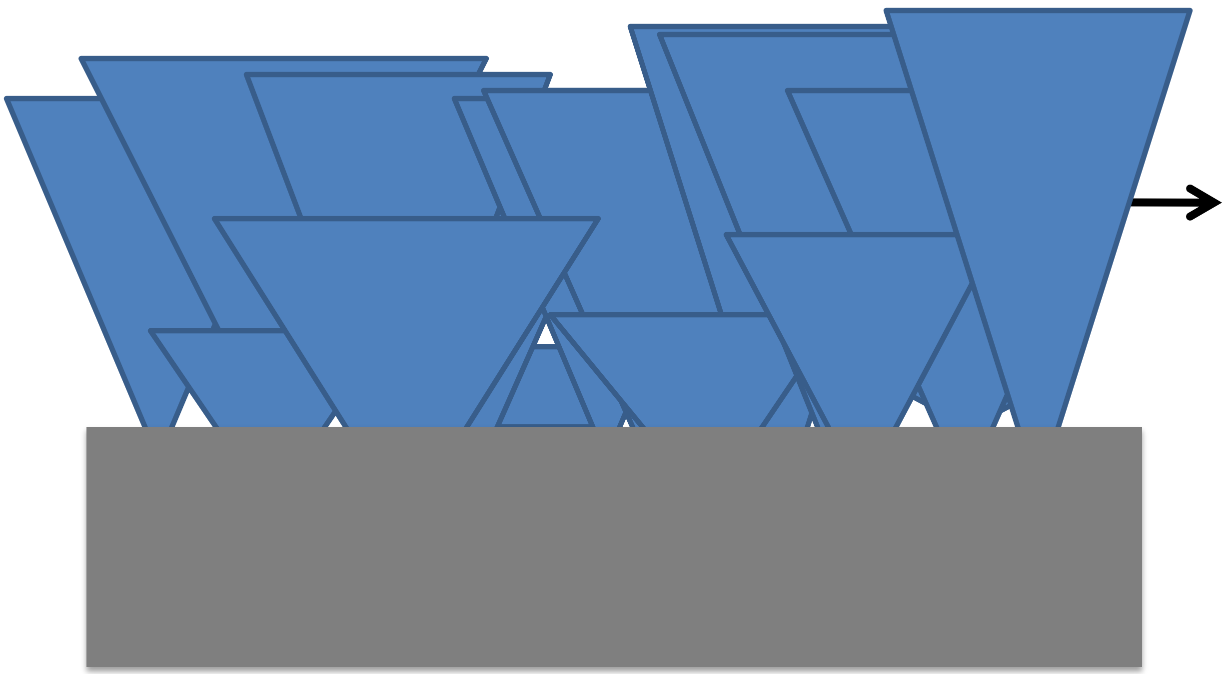
Diamond growth: CVD (growth)

Polycrystalline diamond: *microcrystalline diamond*



Diamond growth: CVD (growth)

Polycrystalline diamond: *microcrystalline diamond*



Microcrystalline diamond
(from 500 nm grains)

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Outline

- Diamond
- Diamond growth
- Intrinsic NCD layers
- Boron-doped NCD

Intrinsic NCD layers

Undoped nanocrystalline diamond layers

Higher quality obtained by:

1. Increasing film thickness

   AND/OR

2. Decreasing C/H-ratio

Larger grains → less grain boundaries

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Intrinsic NCD layers

Nanocrystalline diamond layers

Intrinsic NCD layers

Nanocrystalline diamond layer

Higher quality obtained by:

1. Increasing film thickness → Fixed Thickness

   AND/OR

2. Decreasing C/H-ratio → Change C/H-ratio

Larger grains → less grain boundaries

Higher diamond quality

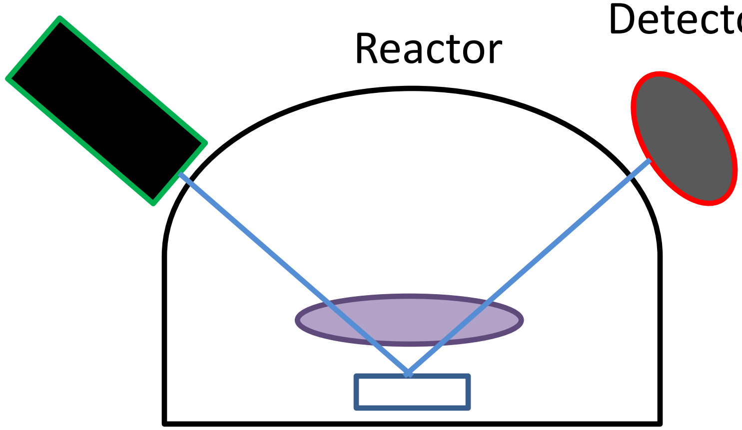
Intrinsic NCD layers

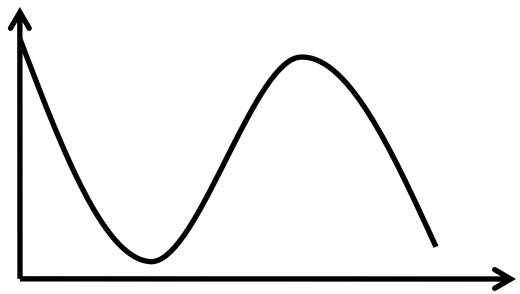
Growth Conditions

- Temperature: 775 °C
- Microwave Power: 3500 Watt
- Pressure: 27 hPa (20 torr)
- Thickness: 150 nm
- C/H-ratio: 0.5%, 1%, 2%, 4%, 8%

Intrinsic NCD layers

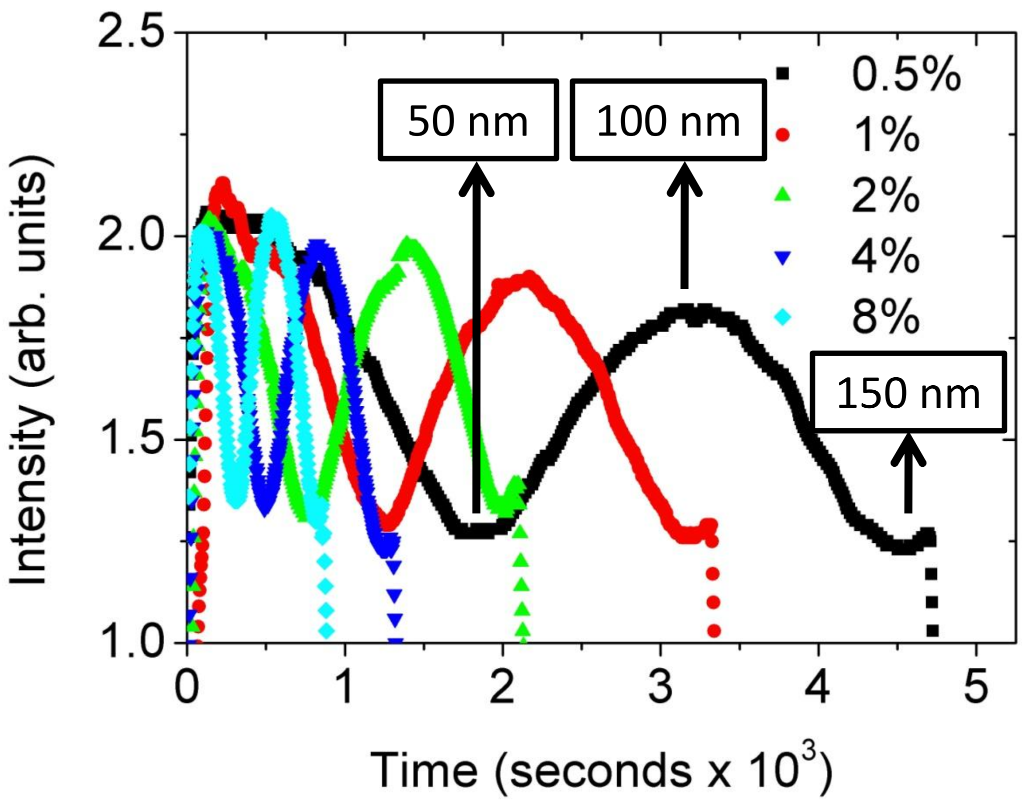
Thickness: Laser interference during growth





Intrinsic NCD layers

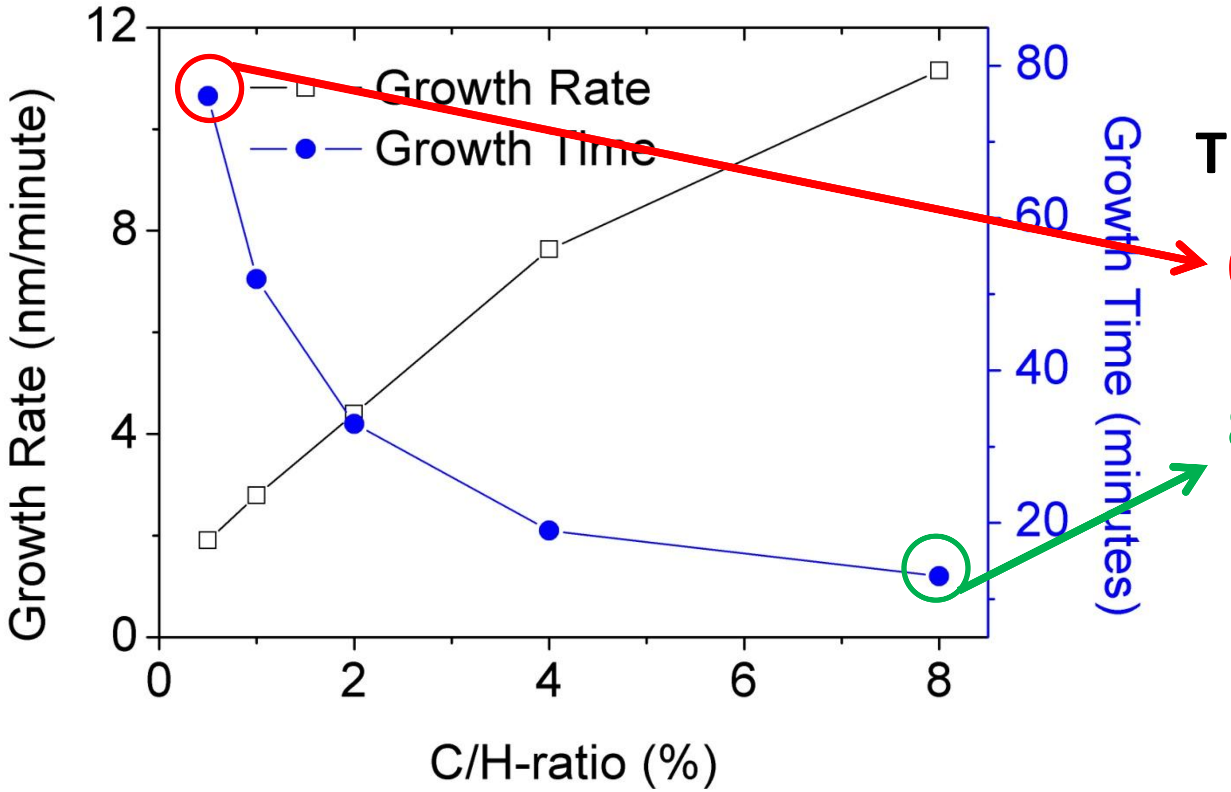
Thickness: Laser interference during growth



Interference:
Every 50 nm
3 X 50 nm = 150 nm

Intrinsic NCD layers

Growth Time



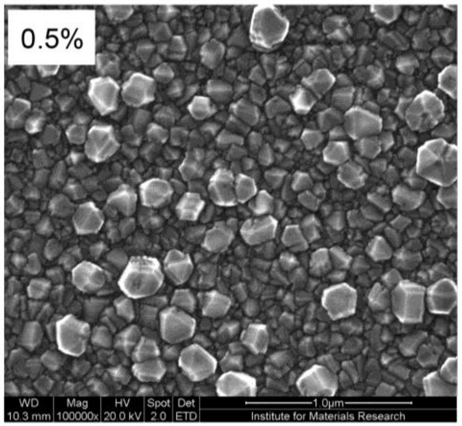
Thickness of 150 nm:

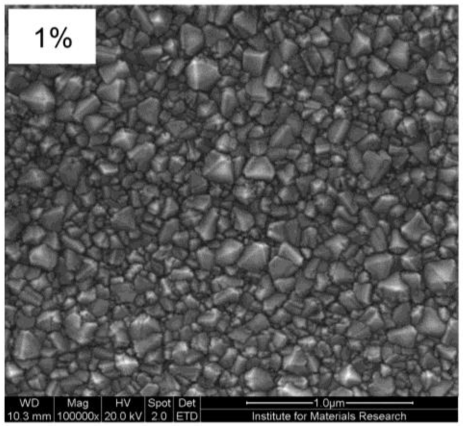
0.5% C/H-ratio → 80 min.

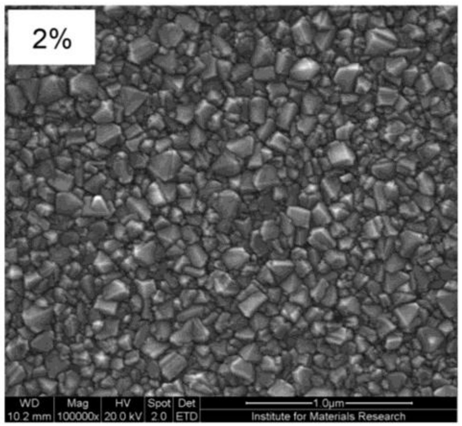
8% C/H-ratio → 12 min.

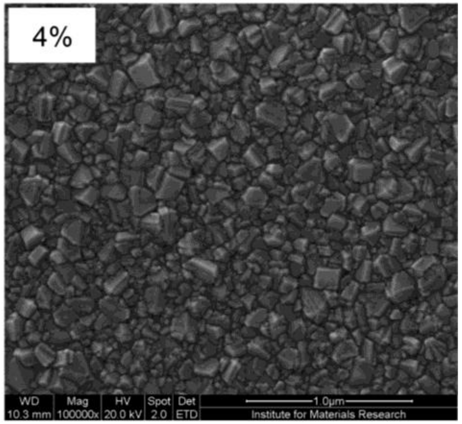
Intrinsic NCD layers

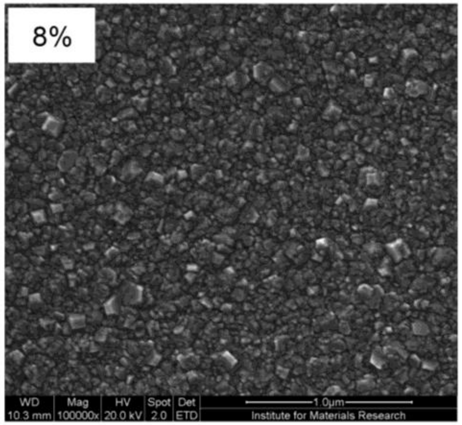
Scanning Electron Microscopy











Grains become smaller with higher C/H-ratio
→ decrease in quality?

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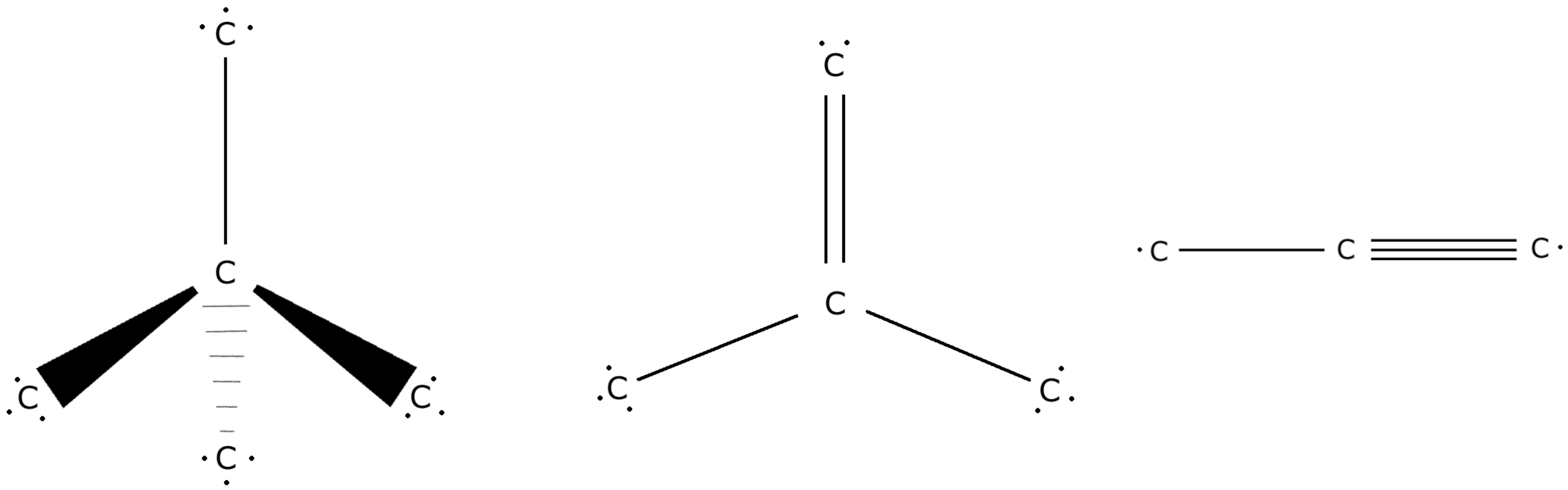
Intrinsic NCD layers

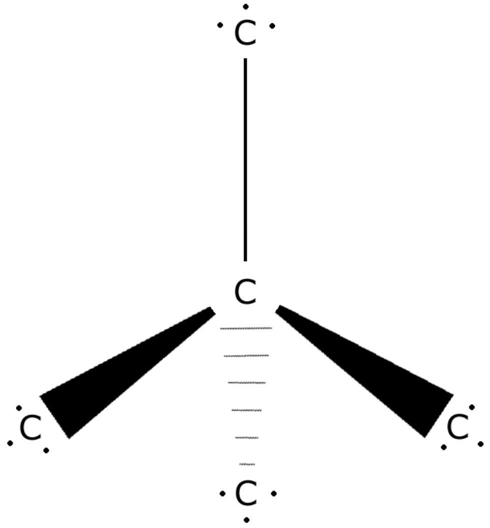
Raman spectroscopy

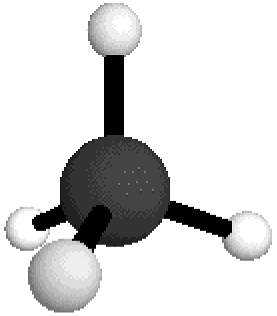


Sensitive for vibrations of carbon atom bonds

Intrinsic NCD diamond layers

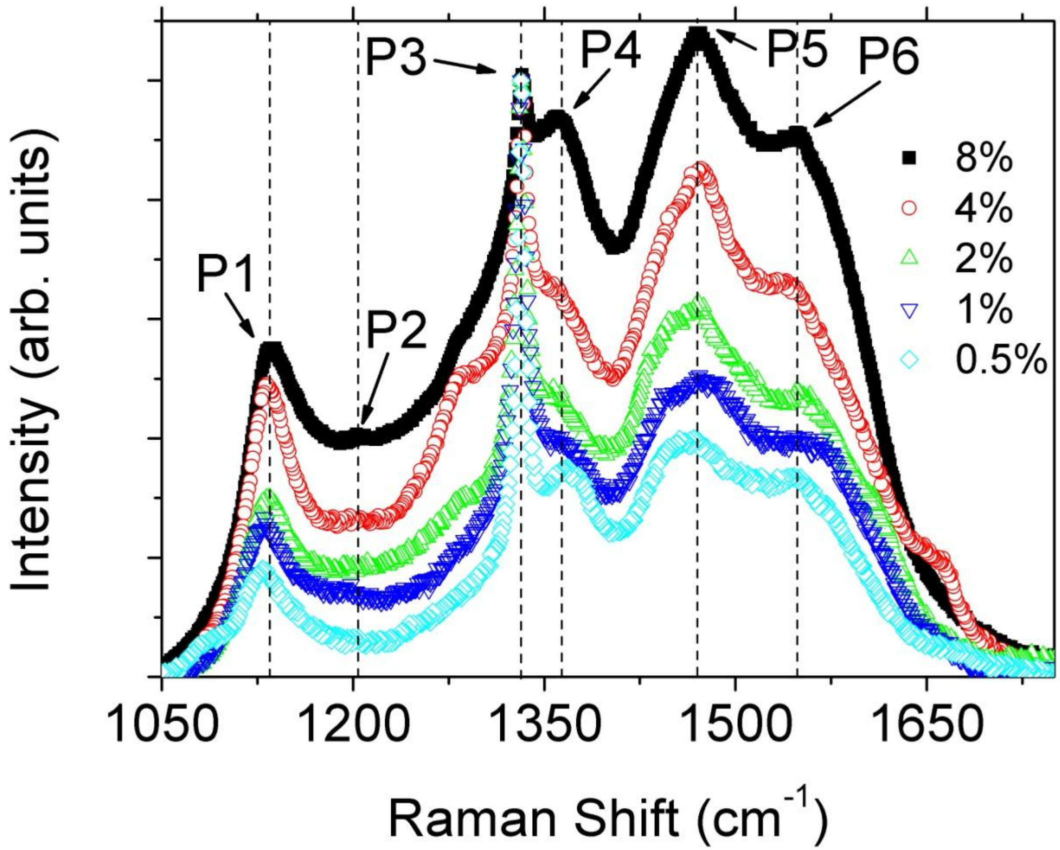
Raman spectroscopy





Intrinsic NCD layers

Raman spectroscopy



P3 = diamond peak
Rest = non-diamond peaks

Increase of diamond peak and decrease in other peaks when decreasing the methane concentration from 8% to 0.5%

Intrinsic NCD diamond layers

Conclusion

Growth with lower C/H-ratio

1. Longer growth time
2. Larger grains
3. Higher diamond quality

Outline

- Diamond
- Diamond growth
- Intrinsic NCD layers
- Boron-doped NCD

Boron-doped NCD

Heavily boron-doped NCD

Growth with lower C/H-ratio

1. Longer growth time
2. Larger grains
3. Higher diamond quality
4. Boron incorporation?
5. Electronic properties?

(1–3) Intrinsic diamond

(4–5) Janssens et al., New J. Phys. **13**, 083008 (2011)

Boron-doped NCD

Diamond vs. Silicon

Single crystals

- Electronic transport models similar
  - Same amount of Valence Electrons
  - Same Crystal Lattice

Polycrystalline

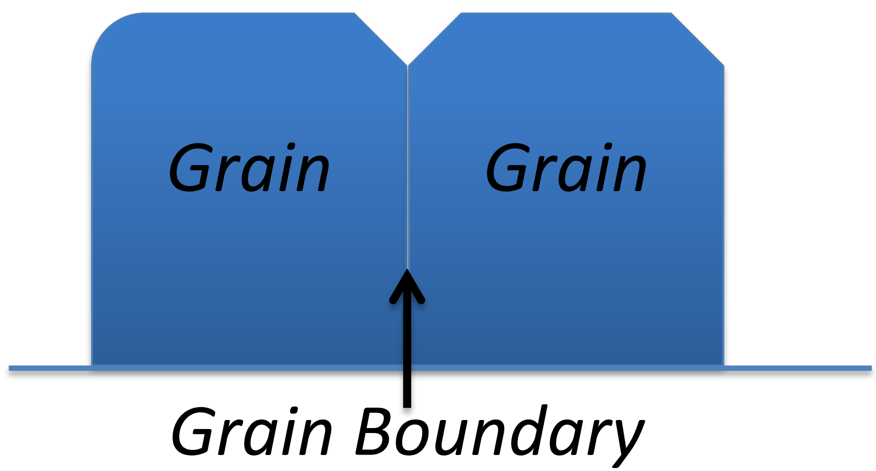
- Influence of grain boundaries on Electromagnetic Transport Properties?

Doped polycrystalline silicon

Morphology vs. electromagnetic transport:

- Lu N C, et al. 1981 *IEEE Trans. Electron Devices* **28** 818

$$\rho = \rho_{GB}\left(\frac{2w}{d}\right) + \rho_{SC}\left(1 - \frac{2w}{d}\right)$$



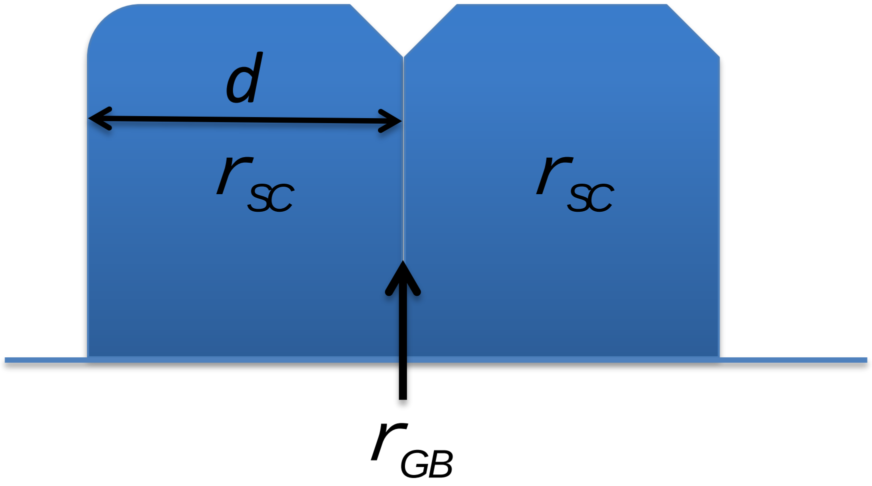
Doped polycrystalline silicon

Morphology vs. electromagnetic transport:

- Lu N C, et al. 1981 *IEEE Trans. Electron Devices* **28** 818

$$\rho = \rho_{GB}\left(\frac{2w}{d}\right) + \rho_{SC}\left(1 - \frac{2w}{d}\right)$$

$2w \approx$ width GB for metallic doping



Doped polycrystalline silicon

Morphology vs. electromagnetic transport:

- Lu N C, et al. 1981 *IEEE Trans. Electron Devices* **28** 818

$$\rho = \rho_{GB}\left(\frac{2w}{d}\right) + \rho_{SC}\left(1 - \frac{2w}{d}\right) \qquad \frac{1}{\mu} = \frac{1}{\mu_{GB}}\left(\frac{2w}{d}\right) + \frac{1}{\mu_{SC}}\left(1 - \frac{2w}{d}\right)$$

Set of samples

d (variable) ➔ varying C/H-ratio

ρ_{SC} and μ_{SC} (constant) ➔ high B-concentration

2w approx. constant ➔ high B-concentration

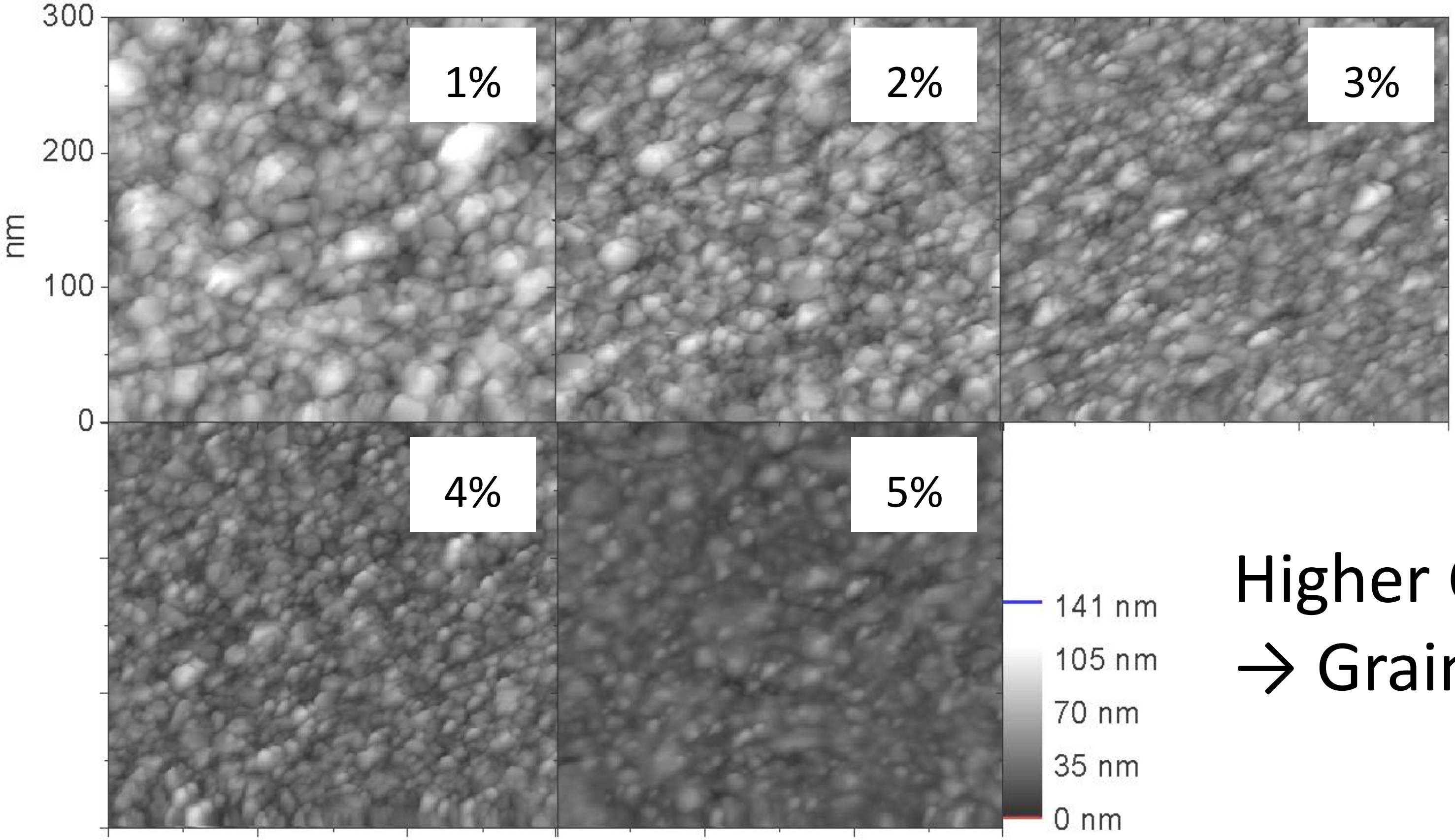
Heavily-doped B:NCD

Growth Conditions

- Temperature: 700 °C
- Microwave Power: 3500 Watt
- Pressure: 33.3 hPa (25 torr)
- Thickness: 150 nm
- C/H-ratio: 0.5%, 1%, 1.5%, 2%, 2.5%, 3%, 3.5% 4%, 4.5%, 5%
- **B/C-ratio: 5000 ppm**

Heavily-doped B:NCD

Morphology: Atomic force microscopy

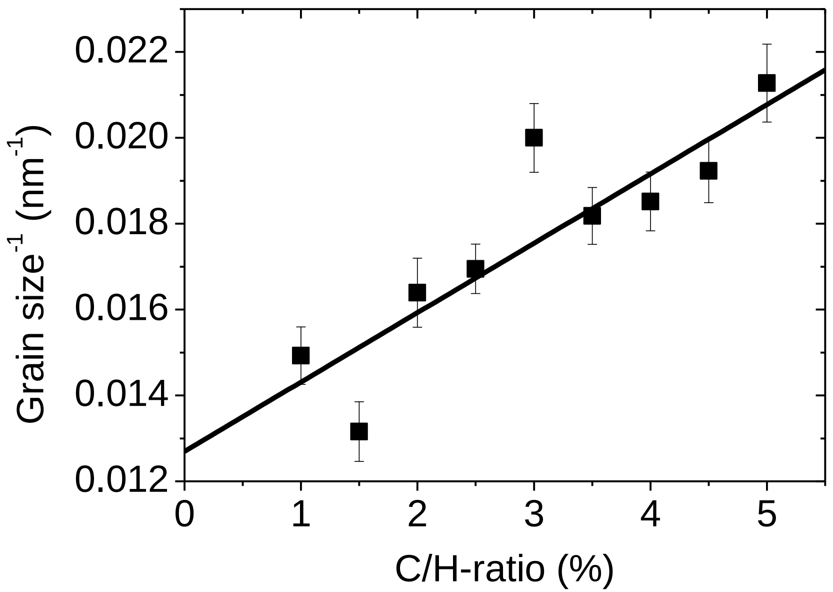


Higher C/H-ratio
→ Grain size ↓

Heavily-doped B:NCD

Morphology: X-ray diffraction (*Scherrer equation*)

C/H-ratio (%)	Grain size (nm)
1	67
1.5	76
2	61
2.5	59
3	50
3.5	55
4	54
4.5	52
5	47



Derived from May et al.:

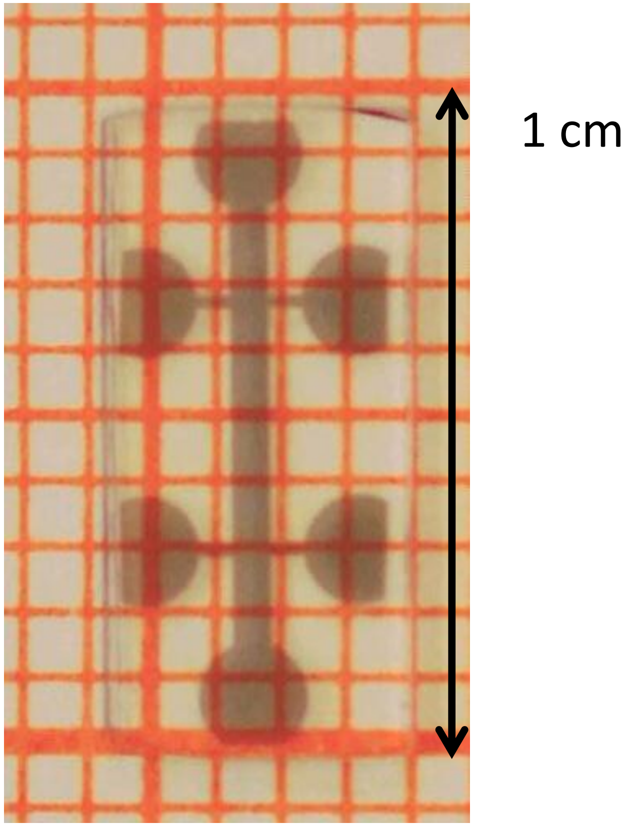
$$\frac{1}{d} = A_d\xi + B_d = A_d\xi + \frac{1}{d_0}$$

May et al., J. Appl. Phys. **101**, 053115 (2007)

Heavily-doped B:NCD

Processing of samples: electronic measurements

- **Hall bar shapes:**
  - Protective Al mask
    (lift off photolithography)
  - Oxygen plasma etch
    (3 min, 300 W, 5.6 x 10-3 mbar)
- **Contacts:**
  - Magnetron sputtered Ti/Al
    (50 nm/200 nm)



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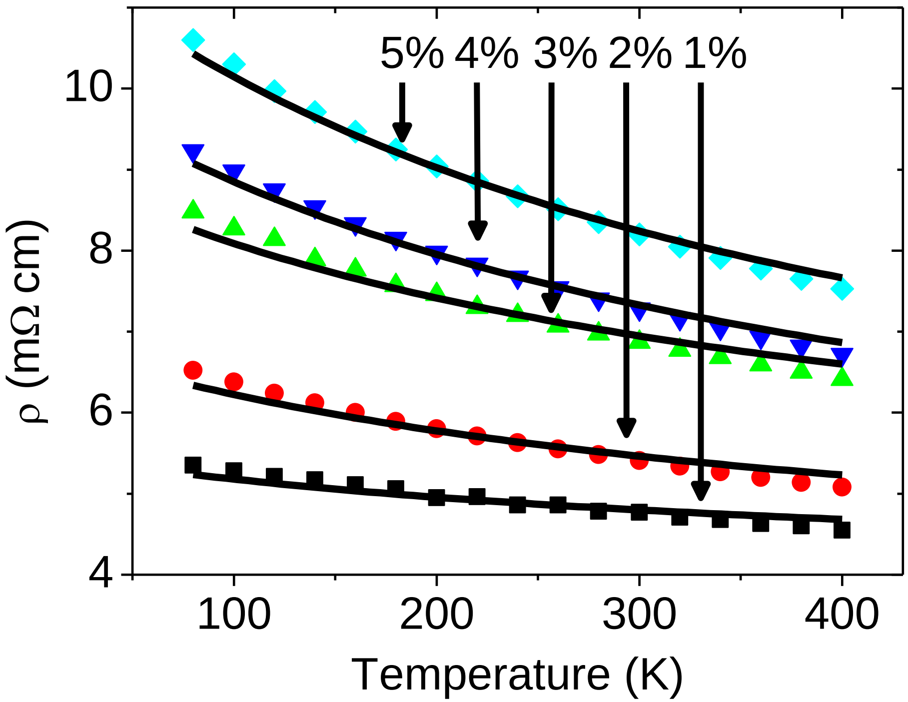
Heavily B:NCD

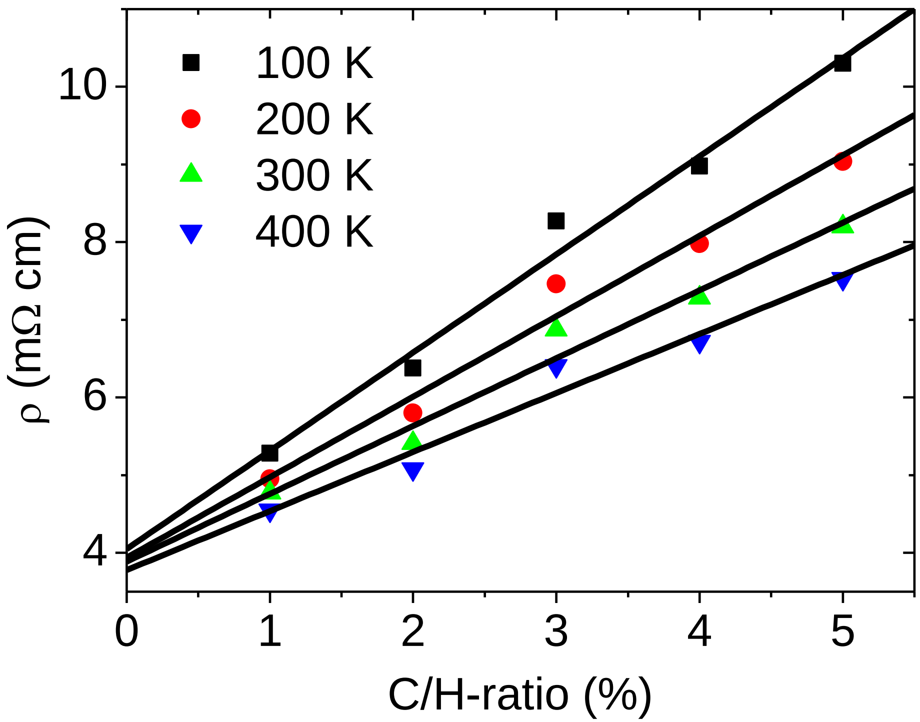
Electronic properties: resistivity = ρ ÷ 1/(n μ)



1. Resistivity:
   5% > ... > 1%
2. T-dependence:
   5% > ... > 1%
3. *Intuitive explanation: grain boundaries induce a higher resistivity*

Heavily B:NCD

Electronic properties: resistivity



1. Plot:
   ρ as a function of C/H-ratio for all temperatures
2. Approximation:
   Linear dependence for all temperatures

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INSTITUUT VOOR MATERIAALONDERZOEK

Heavily B:NCD

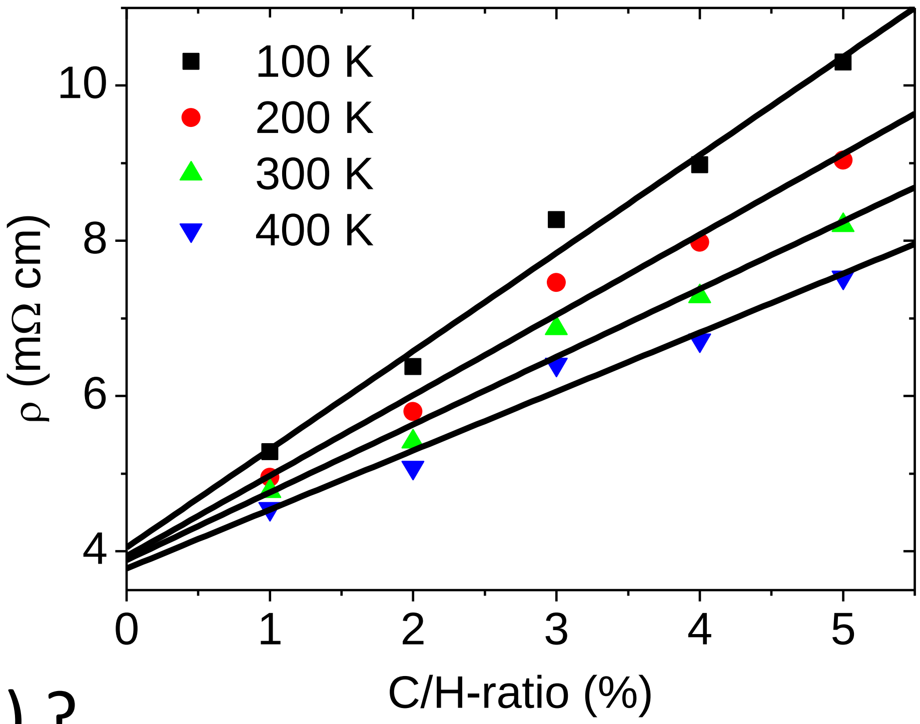
Electronic properties: resistivity

$$\rho = \rho_{GB}\left(\frac{2w}{d}\right) + \rho_{SC}\left(1 - \frac{2w}{d}\right)$$

$$\frac{1}{d} = A_d\xi + B_d = A_d\xi + \frac{1}{d_0}$$

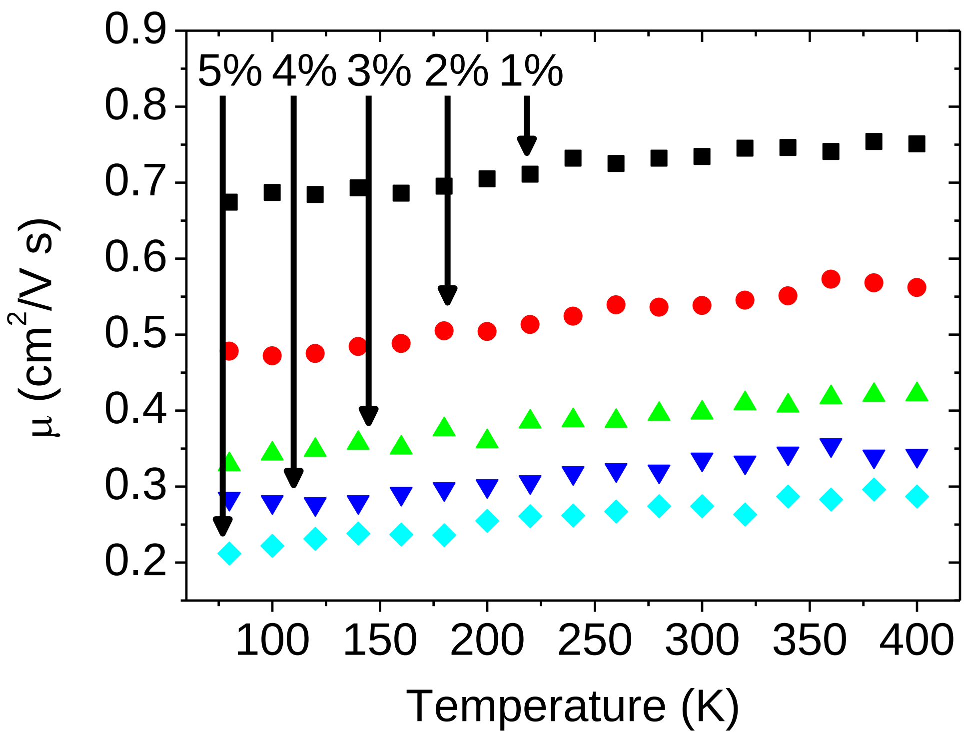
Behavior can be explained

T-dependence ➔ρ ÷ 1/(n μ) ?



Heavily B:NCD

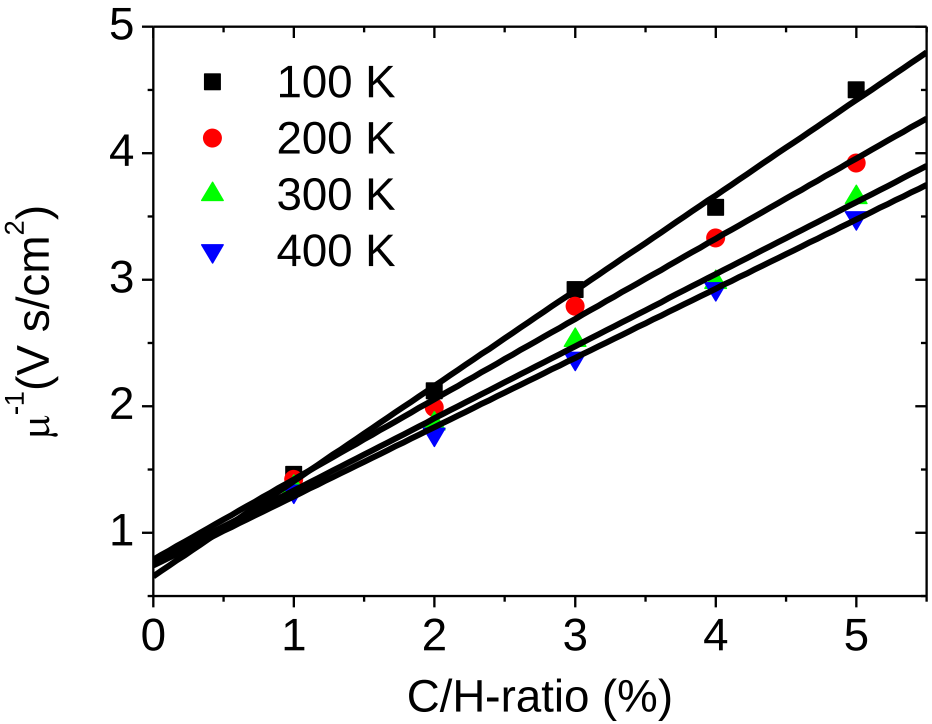
Electronic properties: mobility



1. Mobility (μ):
   1% > ... > 5%
2. T dependence:
   μ increases with T
3. *Intuitive explanation: grain boundaries scatter*

Heavily B:NCD

Electronic properties: mobility



1. Plot:
   μ^{-1} as a function of C/H-ratio for all temperatures
2. Approximation:
   Linear dependence for all temperatures

Heavily B:NCD

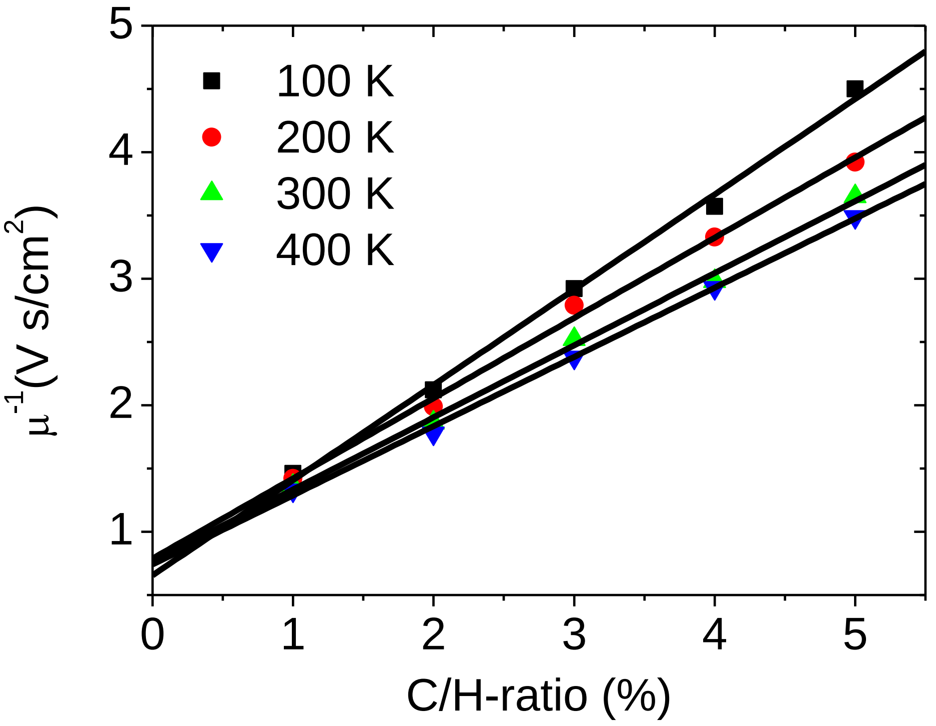
Electronic properties: mobility

$$\frac{1}{\mu} = \frac{1}{\mu_{GB}}\left(\frac{2w}{d}\right) + \frac{1}{\mu_{SC}}\left(1 - \frac{2w}{d}\right)$$

$$\frac{1}{d} = A_d\xi + B_d = A_d\xi + \frac{1}{d_0}$$

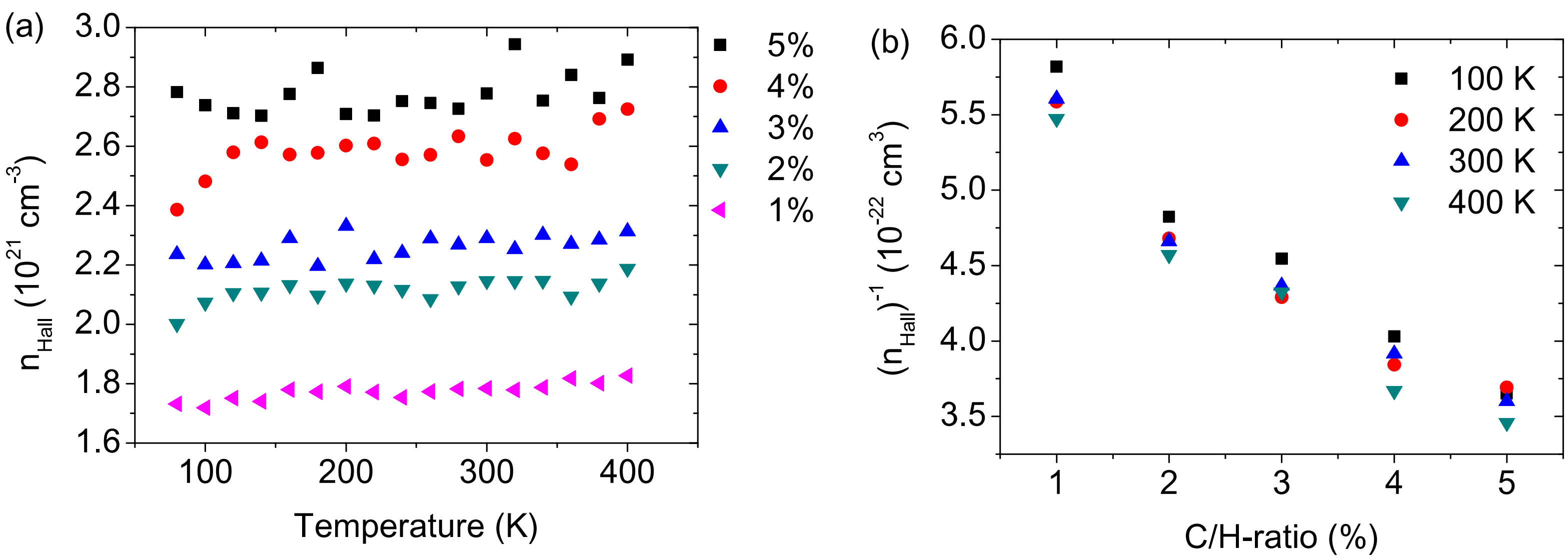
Behavior can be explained

T-dependence of mobility?



Heavily B:NCD

Electronic properties: charge carrier density



Behavior can be explained by more B-incorporation as a function of C/H ratio.

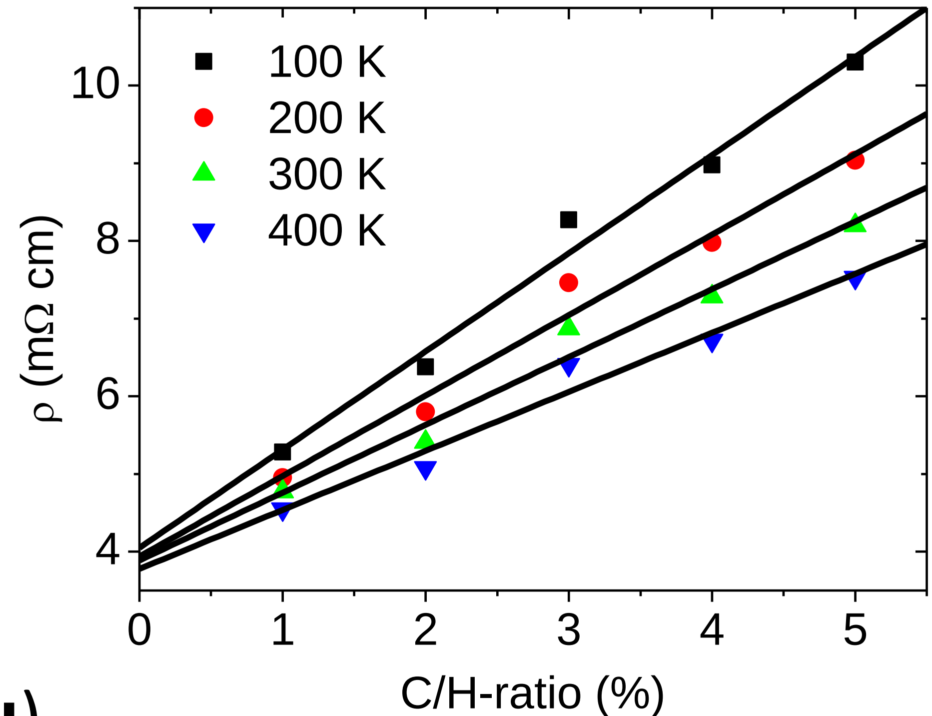
No observed T-dependence for C/H-ratio

Heavily B:NCD

Electronic properties: resistivity

$$\rho = \rho_{GB}\left(\frac{2w}{d}\right) + \rho_{SC}\left(1 - \frac{2w}{d}\right)$$

$$\frac{1}{d} = A_d\xi + B_d = A_d\xi + \frac{1}{d_0}$$



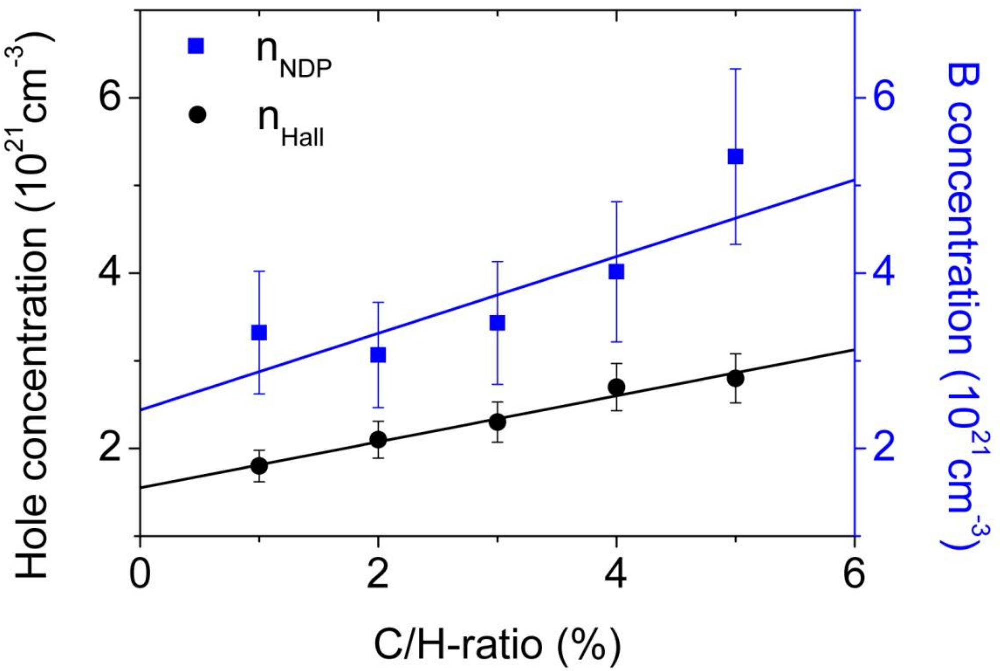
Behavior can be explained

T-dependence ➔ ρ ÷ 1/(n **μ**)

Heavily B:NCD

Active and total boron concentration:

- Active [B] from Hall effect measurements (n_{Hall})
- Total [B] from neutron depth profiling (n_{NDP})



With increasing C/H-ratio

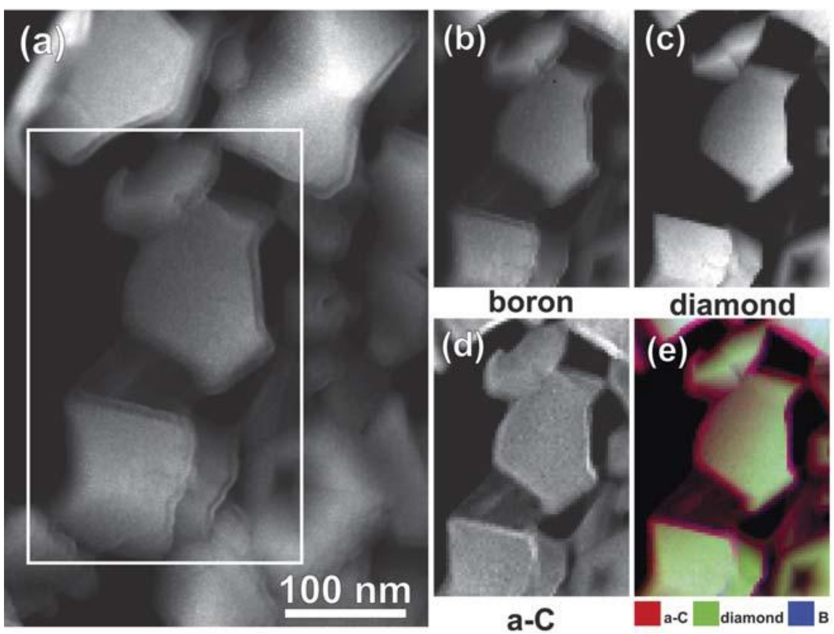
1. Increase in boron incorporation
2. More and more inactive boron incorporation

50-70% active incorporated (@ 400K)

Heavily B:NCD

Active and total boron concentration:

- Nanoscopic investigation with TEM and EELS



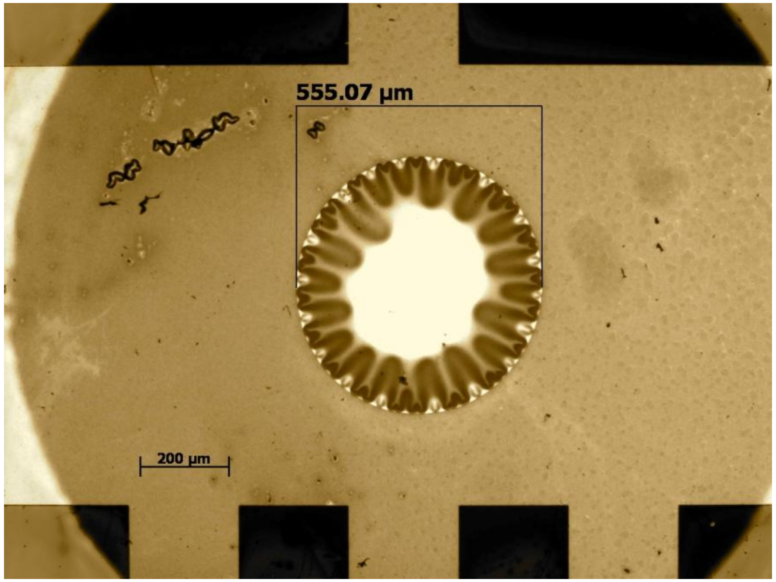
No preferential B-incorporation

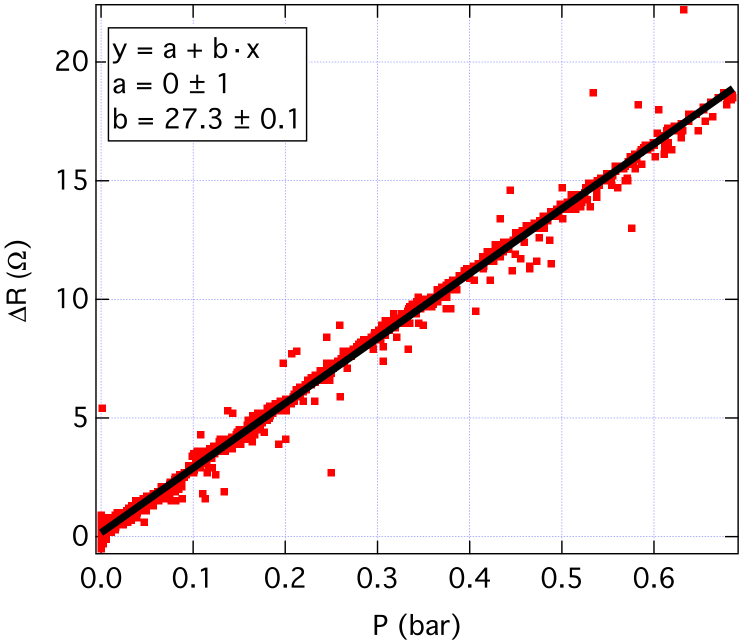
S. Turner et al. Nanoscale, 2012, 4, 5960

Heavily B:NCD

Piezoresistive properties

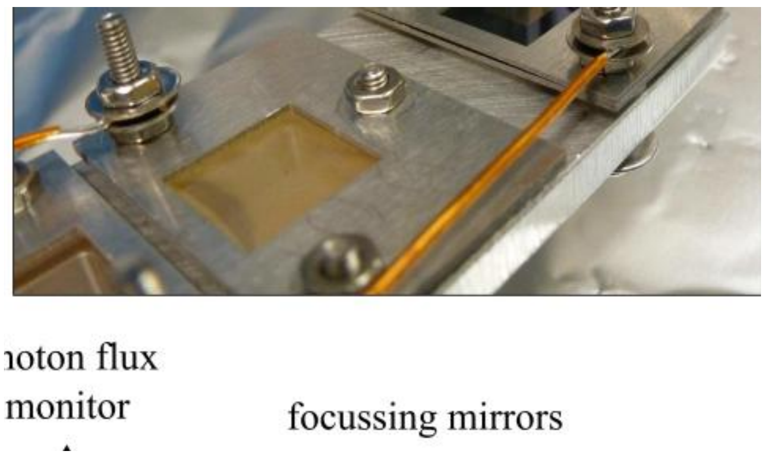
- 150 nm thick B-NCD membrane on glass, in the middle of a Hall bar structure (to be published).

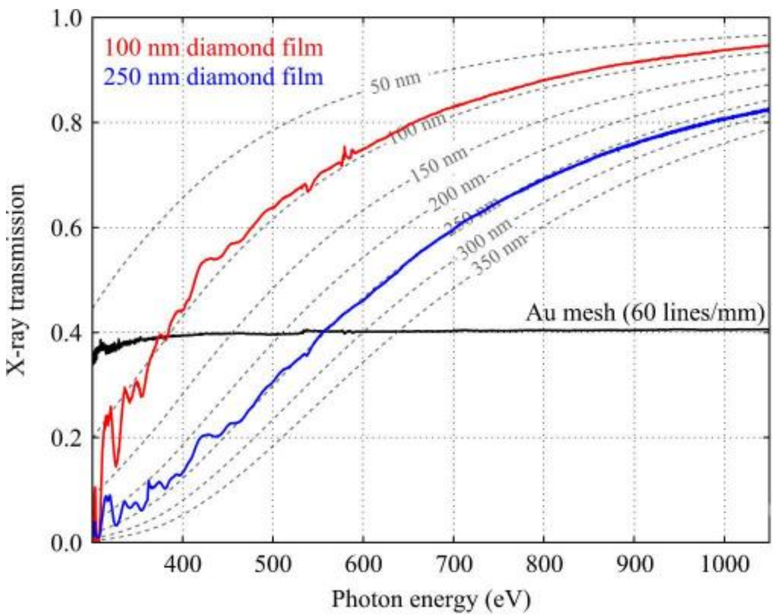




Heavily B:NCD

Soft X-ray detectors





100 and 250 nm thick diamond membranes on silicon (0.5 mm by 0.5 mm)

K. Kummer et al. Review of Scientific Instruments 2013, 84, 035105

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- Matcon Molesol project