Growth and properties of (ultra) nano crystalline diamond

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- Nano-related research at the Technische Universtität München:
  more than 50 research groups from
  several faculties and central institutes are
  working on nanoscience and nanotechnology
- Broad range of research topics (theoretical work, fundamental research, applied science, technology)
- Many topics/research fields are interdisciplinary

2004: start of nanoTUM – TUM Institute for Nanoscience and Nanotechnology

- Coordination of all activities in the field of nanoscience/nanotechnology in one virtual institute
- Cross-links to other nano clusters/networks in and around Munich by concomitant members in Clusters of Excellence etc.
- Intensive collaboration with partner universities DTU and TU/e

Chemical vapour deposition (CVD) of diamond

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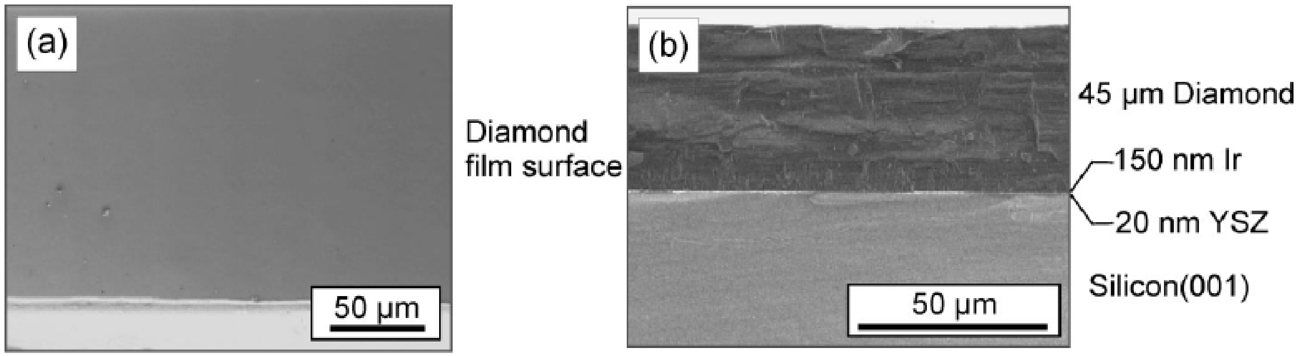
- Gas mixture of carbon containing gas and hydrogen
  e.g. 1-5% CH_4 in H_2
- Formation of radicals and atomic hydrogen by plasma or hot filament
- High enough substrate temperature: diamond deposition
- Role of atomic hydrogen:
  - stabilisation of sp^3 carbon phase
  - etching of sp^2 carbon phase
- Deposition on non-diamond substrates:
  pretreatment required to enhance nucleation density
- Morphology: from monocrystalline to (ultra)nanocrystalline

Monocrystalline CVD diamond films

- Homoepitaxy: diamond substrates
  limited by size of substrates

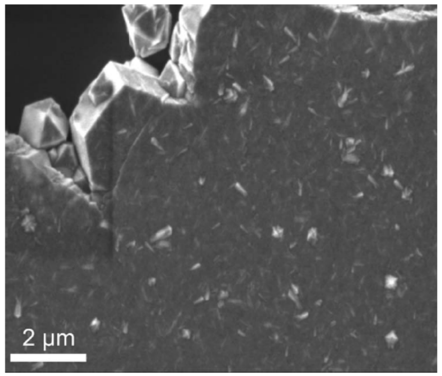
- Heteroepitaxy: bias enhanced nucleation
  Ir/$SrTiO_3$/Si(001) (Schreck et al. 2004)
  Ir/YSZ/Si(001), Ir/YSZ/Si(111) (Schreck et al. 2004, 2008)
  up to 4 inch.

Diamond on Ir/YSZ/Si(001)



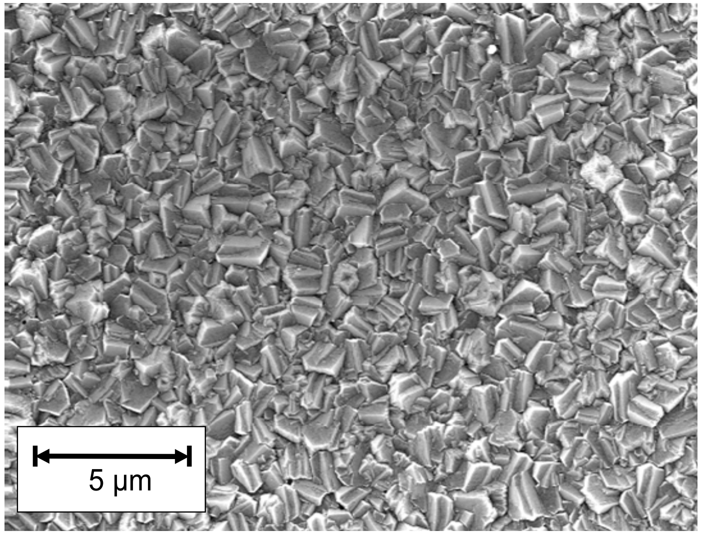
Gsell, Schreck et al. 2004

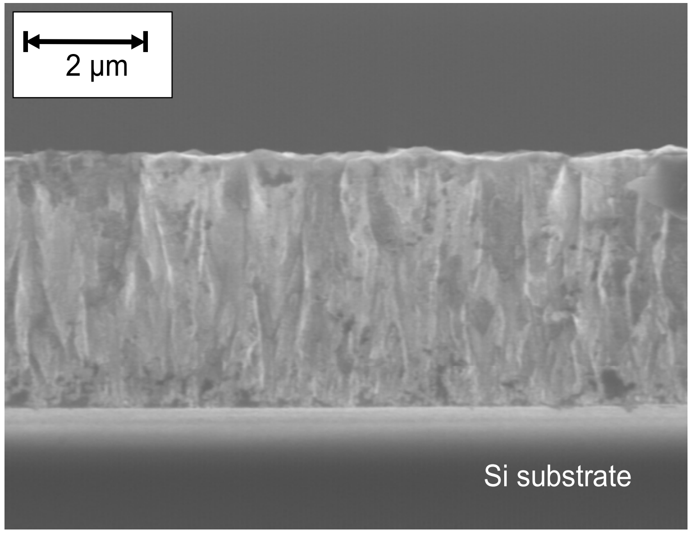
Diamond on Ir/YSZ/Si(111)



Fischer, Schreck et al. 2008

Polycrystalline CVD diamond films





Sternschulte et al. Diamond 2006

- Substrates: Si, SiC, glass, metals (e.g. Ti, Mo, WC) etc
- Columnar growth
- Roughness increases with film thickness

Polycrystalline diamond (PCD) films: Van der Drift growth model

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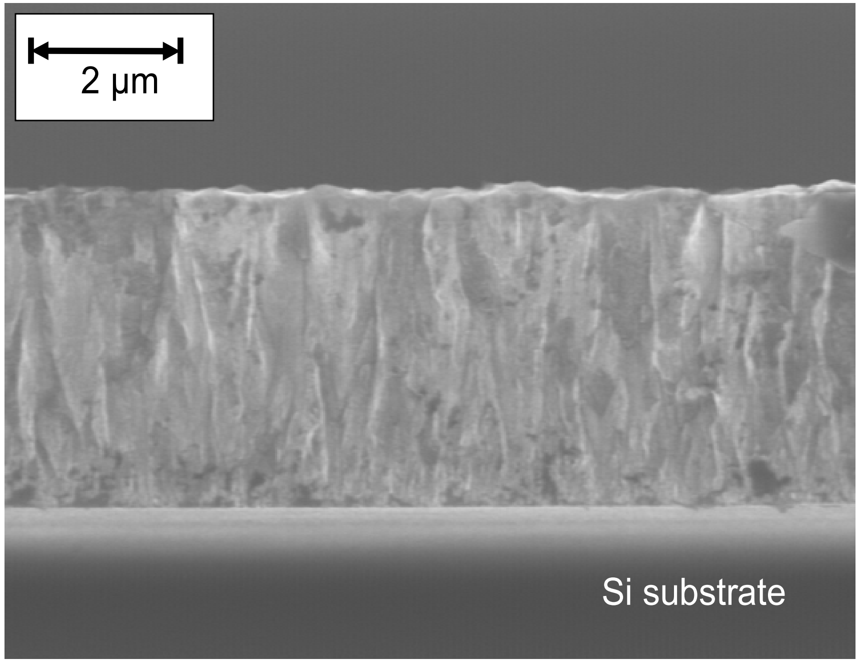
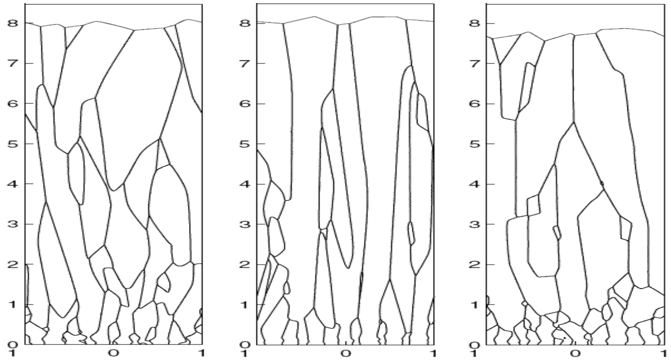


Sternschulte et al. Diamond 2006



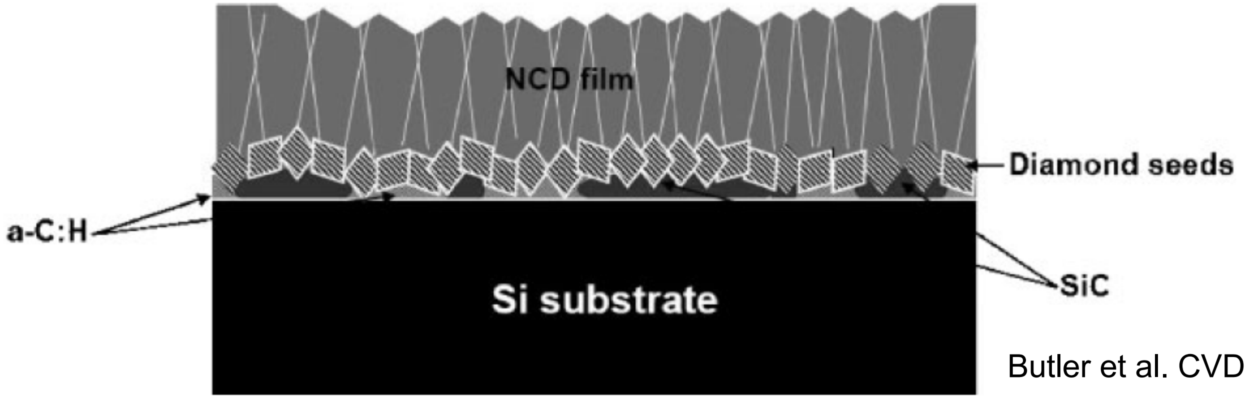
Smereka et al. Acta Materialica 2005

- Van der Drift growth model: overgrowth of crystallites

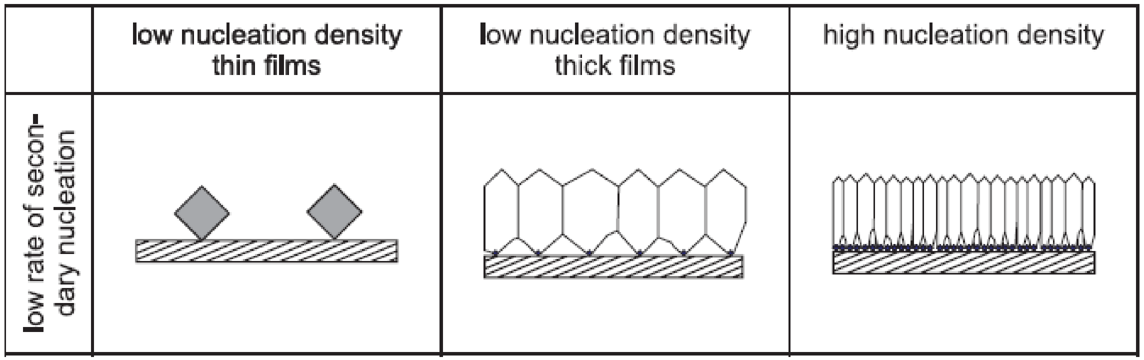
⇒ Development of surface texture depending on fastest growth direction

⇒ Fastest growth direction influenced by growth parameters e.g. by CH_4 concentration, substrate temperature

PCD with short deposition times: "pseudo" nanocrystalline diamond films



Butler et al. CVD 2008



Kulisch et al. phys. stat. sol. (a) 203 (2006) 203

Very high diamond nucleation density on substrate and short deposition times:

$\Rightarrow$ thin fully closed films with small diamond crystallites

grain size (lateral) up to 100nm

But: Anisotropic properties

(Ultra) Nanocrystalline CVD diamond films

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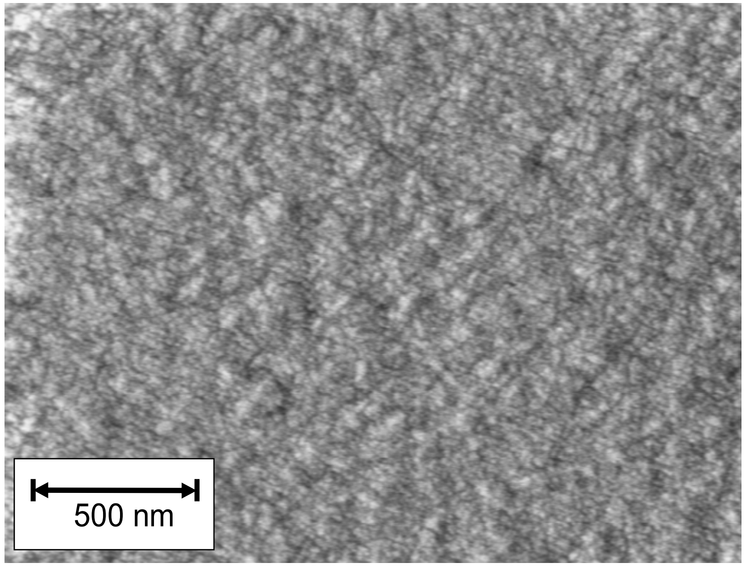

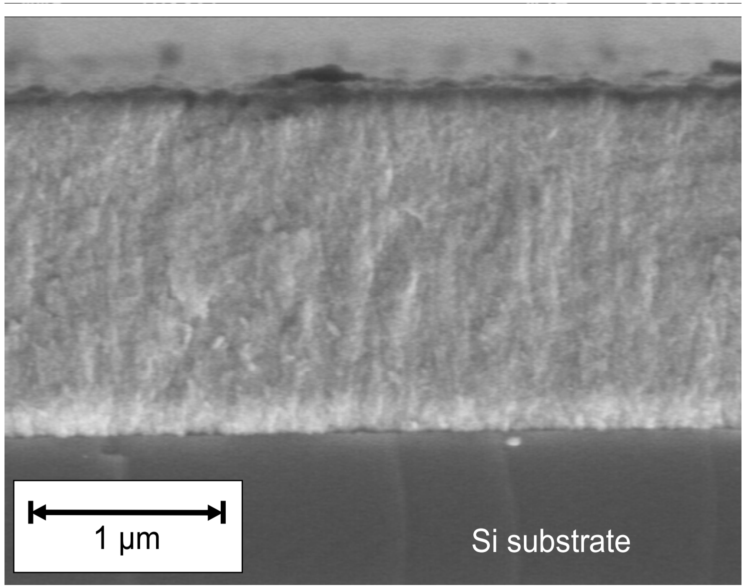

Sternschulte et al. Diamond 2006

- Fine grained material with structureless cross section
- “Homogeneous” material compared to PCD
- Roughness ≈ 10-15nm
  independent from film thickness up to several µm
- Different growth mode

Growth of ultra nano crystalline diamond (UNCD) films

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- CVD with oversaturated carbon precursor concentration
  e.g. by replacement of hydrogen gas by Ar or N_2
  or drastically increased carbon concentration in H_2 gas mixture
- Other possibility: applied bias voltage during growth process

$\Rightarrow$ Generation of high concentrations of defects at the surface

- Defect sites cause formation of twins, nucleation of new crystallites

$\Rightarrow$ Extremely high secondary nucleation rate during diamond deposition

$\Rightarrow$ small diamond grains

- Ultrananocrystalline diamond (UNCD): diamond grains $\leq$10nm
  Nanocrystalline diamond (NCD): diamond grains $\approx$10-100nm

Structural properties of UNCD films

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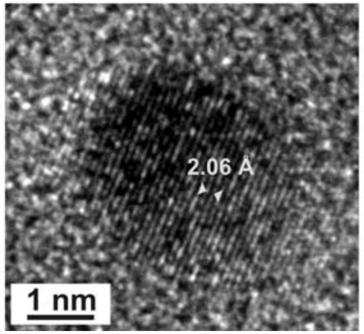
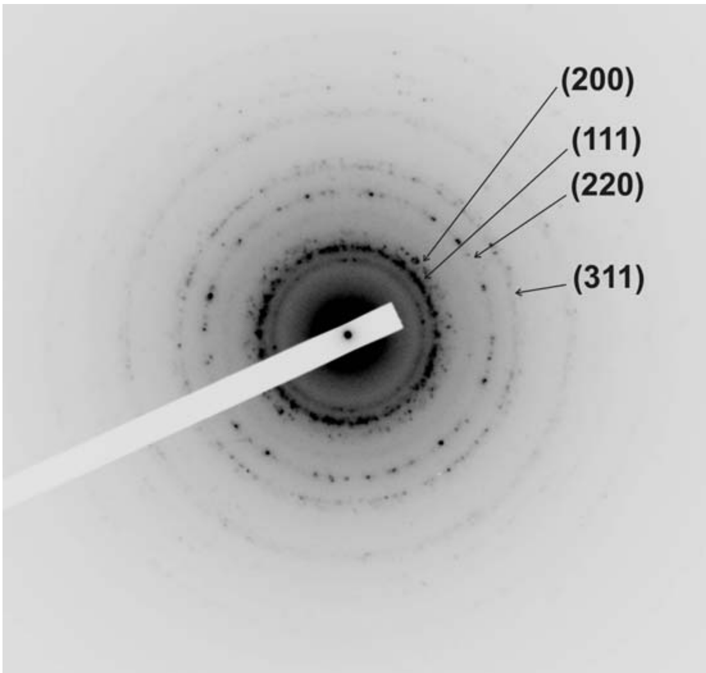
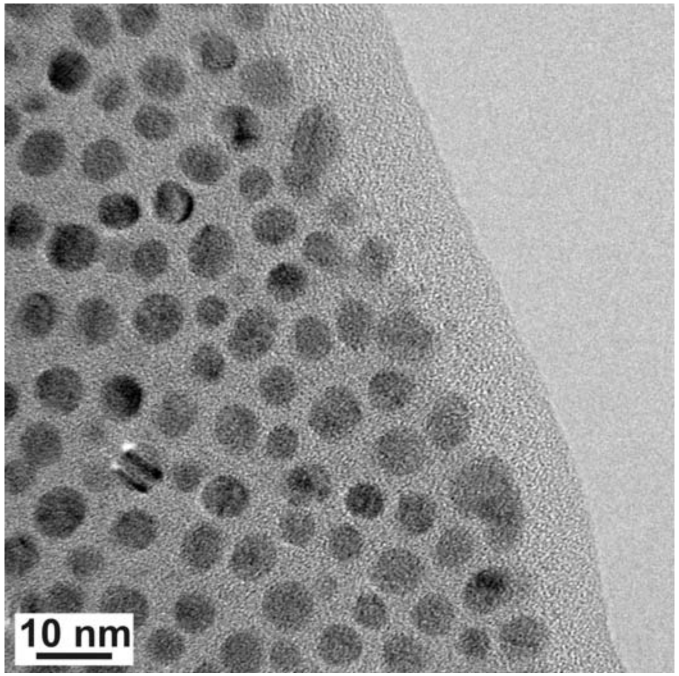
- Small crystalline diamond grains embedded in amorphous sp^2/sp^3 C:H matrix



- No preferred orientation: powder like

$\Rightarrow$ Model system for amorphous materials





TEM: R. Brescia
(Uni Augsburg)

Morphology of UNCD on Si: low nucleation density with $10^8/cm^2$

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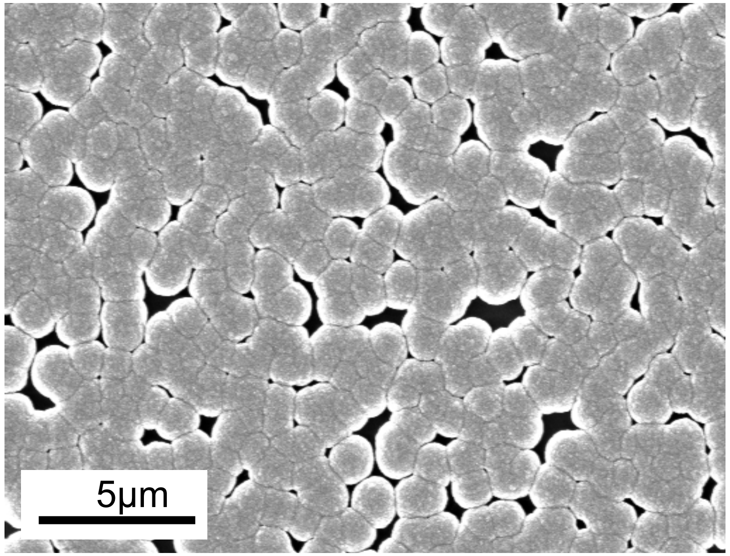

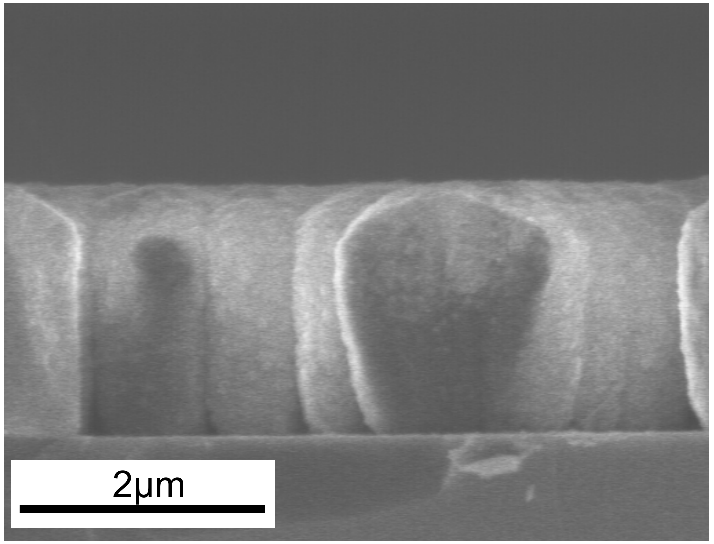

Sternschulte et al., Diamond 2007

- Rough surface with circular shaped diamond islands
- Each sphere consists of nanocrystalline diamond

Growth mechanism

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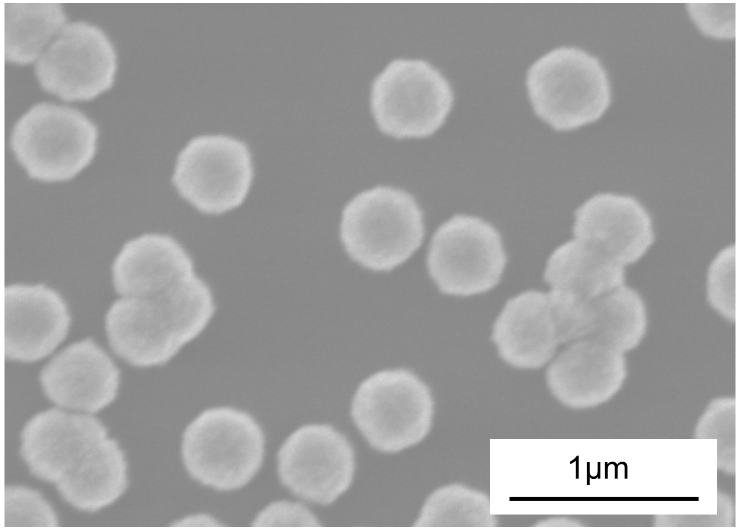
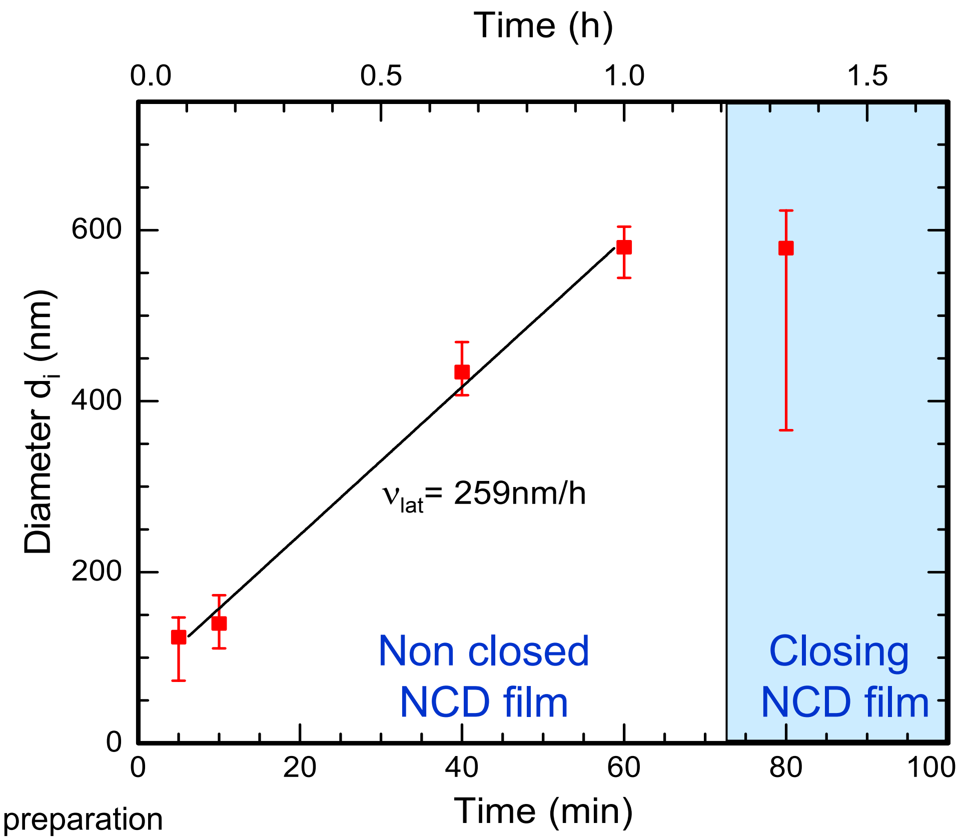
SEM: UNCD with t_{dep}=40min





Sternschulte et al, in preparation

- Diamond island size distribution independent from deposition time

$\Rightarrow$ no diffusion controlled growth

Growth mechanism

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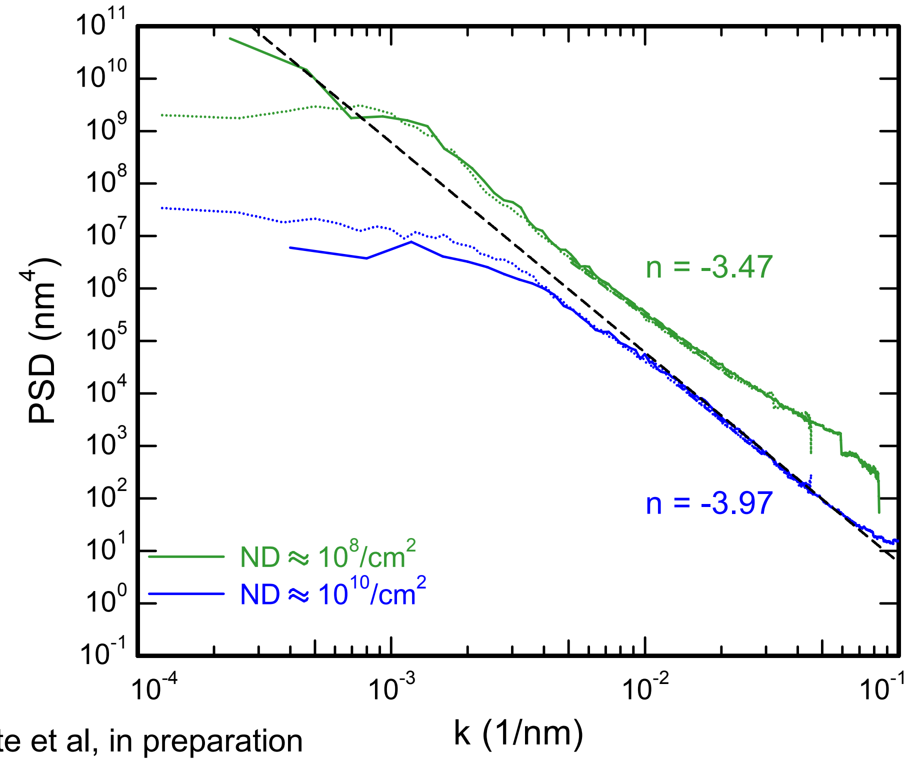
- Growth mechanism:
  growth perpendicular to surface
  (Huygens principle)

⇒ Smoothening via growth and
coalescence of diamond islands

- From PSD analysis of surface roughness:
  Indication for smoothening effect by surface diffusion



Sternschulte et al, in preparation

Properties of UNCD and NCD: how large is the influence of the grain boundaries?

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- UNCD/NCD consists of diamond nano particles embedded in a matrix

$\Rightarrow$ High fraction of atoms located at grain boundaries:

cubic diamond grain with a = 3.6nm: 38% C at surface
a = 36nm: 3.8 % C at surface

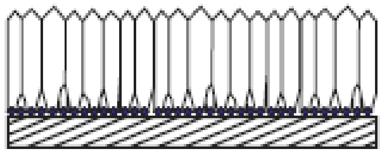
$\Rightarrow$ Small volume fraction of diamond:

grain boundary width 4nm and $\varnothing_{dia}$ = 10nm: 36% of volume is diamond
$\varnothing_{dia}$ = 20nm: 58%
$\varnothing_{dia}$ = 5nm: 17%

- “Number“ of grain boundaries:

UNCD: grain boundaries in 3D: 10nm grain size $\Rightarrow 10^{18}/cm^3$
100nm grain size $\Rightarrow 10^{15}/cm^3$

“pseudo“ NCD with perfect columns: grain boundaries only lateral (2D)
10nm diameter $\Rightarrow 10^{12}/cm^3$



Kulisch et al. (2006)

Properties of UNCD films: sp^2 carbon

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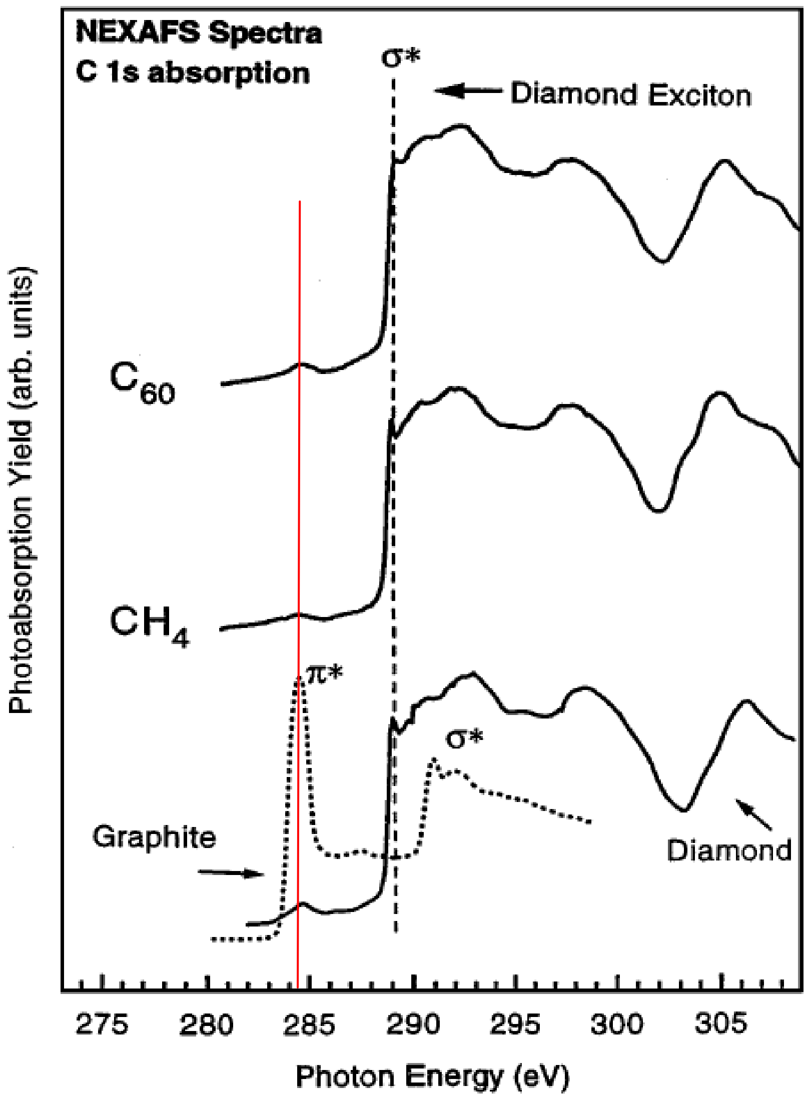

Gruen Annu. Rev. Mater. Sci 1999

- NEXAFS to determine fraction of sp^2 carbon:

  C1s absorption with clearly separated signal of sp^2 and sp^3 C

- In this example: less than 5% sp^2 bonded carbon

- Most probably at the grain boundaries/boundary between grains and matrix

⇒ Influence of grain size on sp^2 concentration

Determination of sp^2 carbon: EELS

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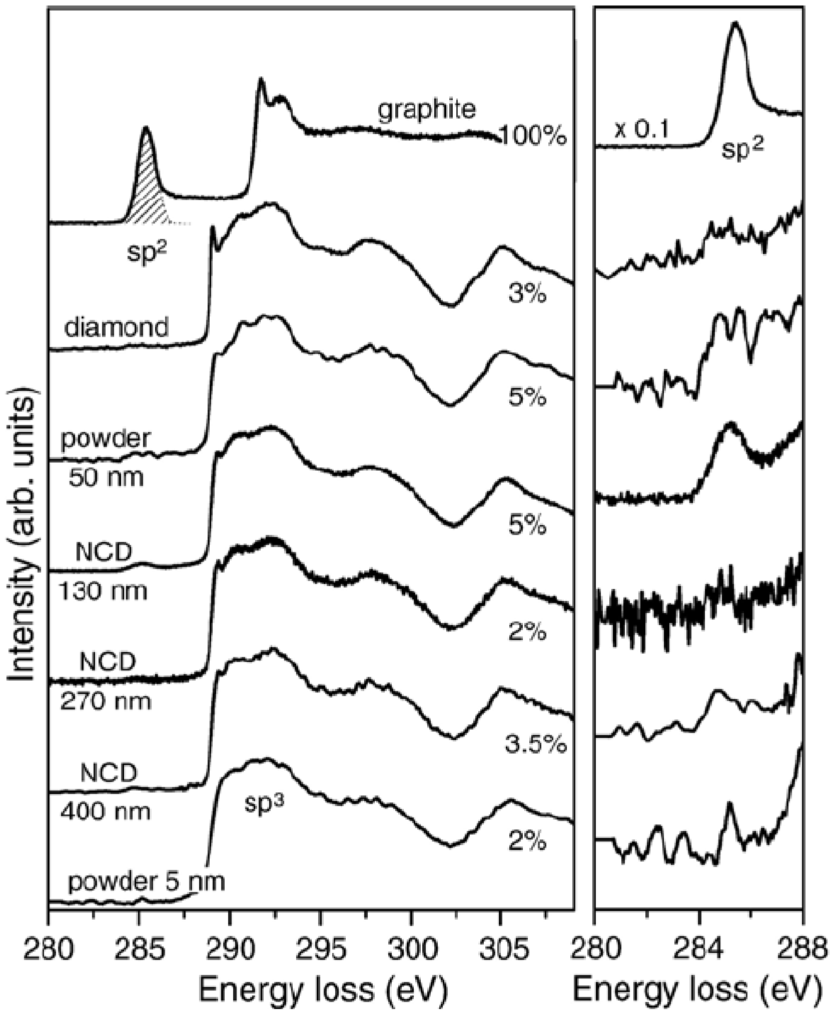

Liu et al. Diamond Relat. Mater. 2007

- Another possibility:
  Energy electron loss spectroscopy (EELS)
- XPS or TEM
- Advantage of TEM: mapping

EELS at TEM:
sp^2 carbon at grain boundaries

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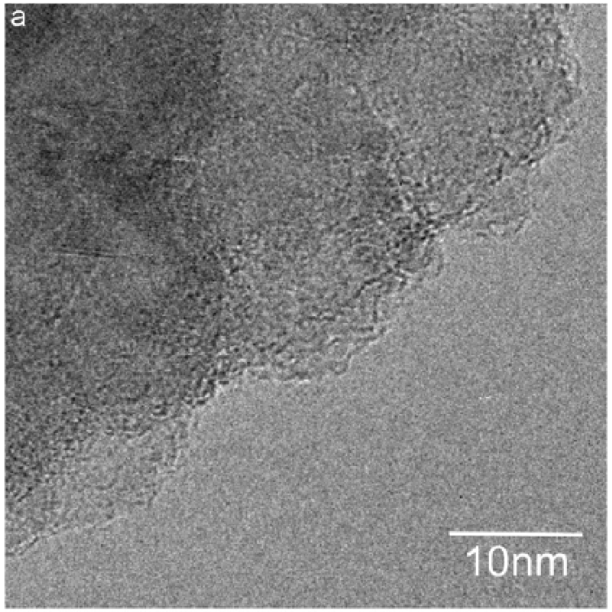

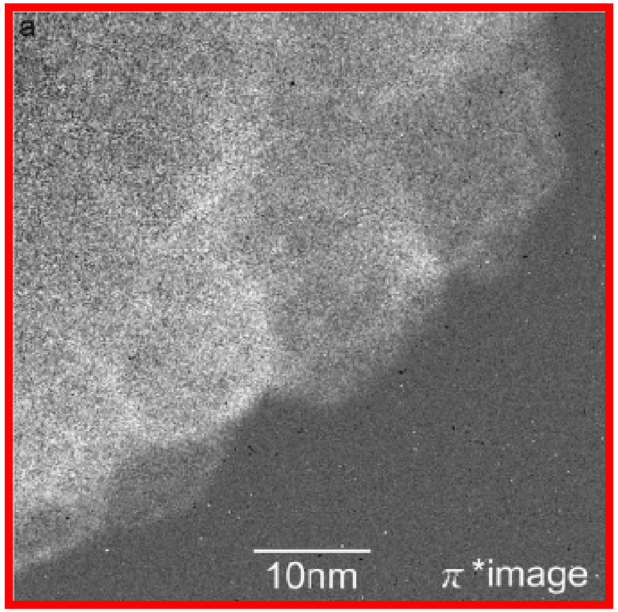

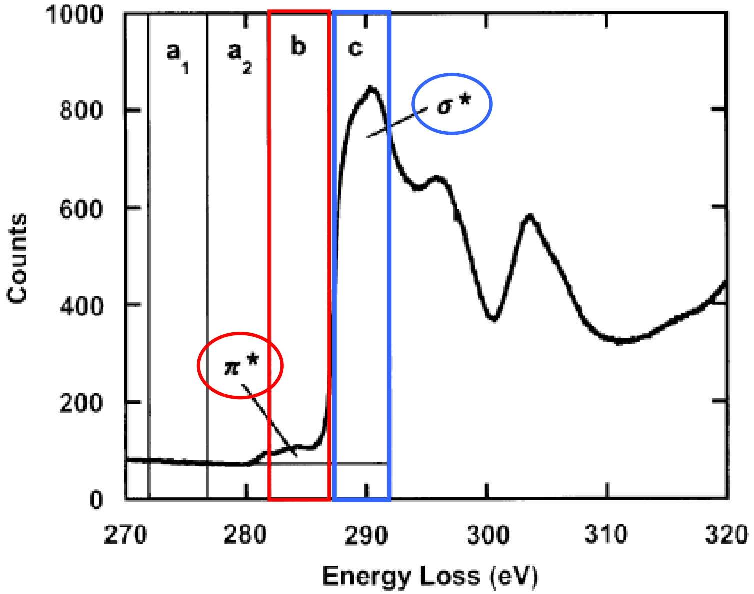

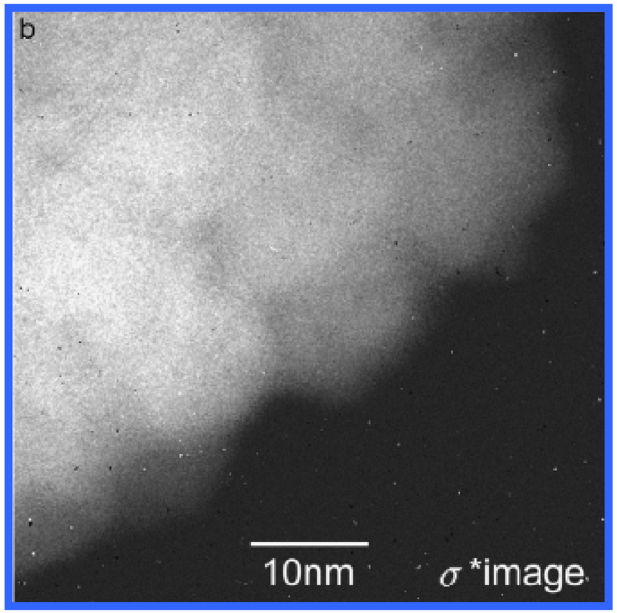

Okada et al.
J. Appl. Phys. 2003

H concentration: IR absorption

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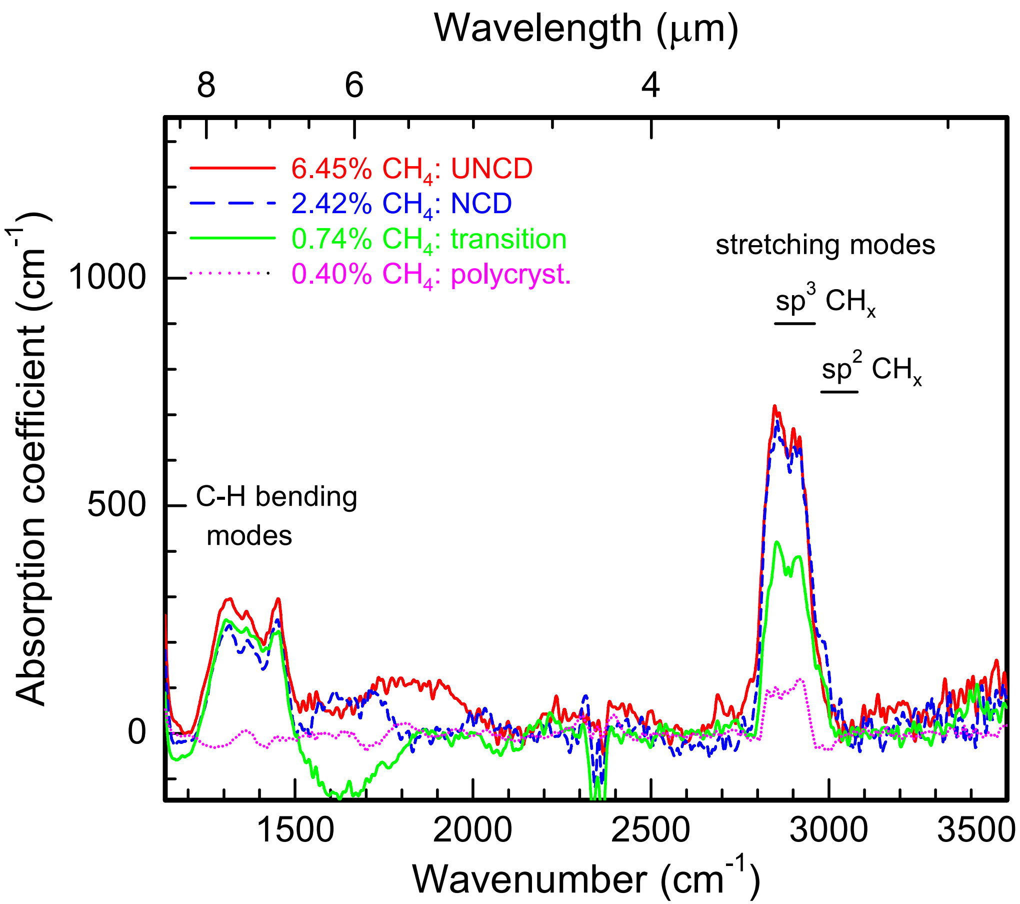
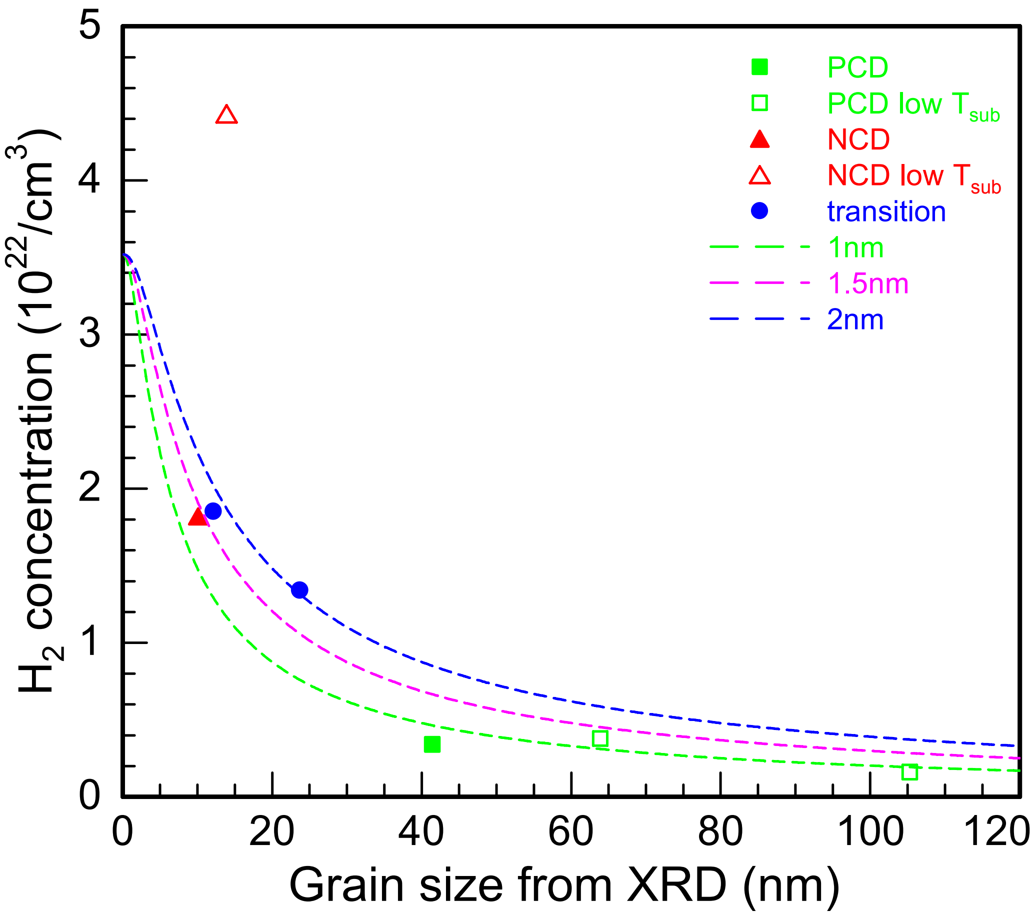


Sternschulte et al. Diamond 2006

- IR absorption shows clear signal of C-H modes
- Measurement of bulk material

H concentration in NCD films



- H concentration scales with grain size

$\Rightarrow$ H is incorporated in the grain boundaries

H incorporation in UNCD films

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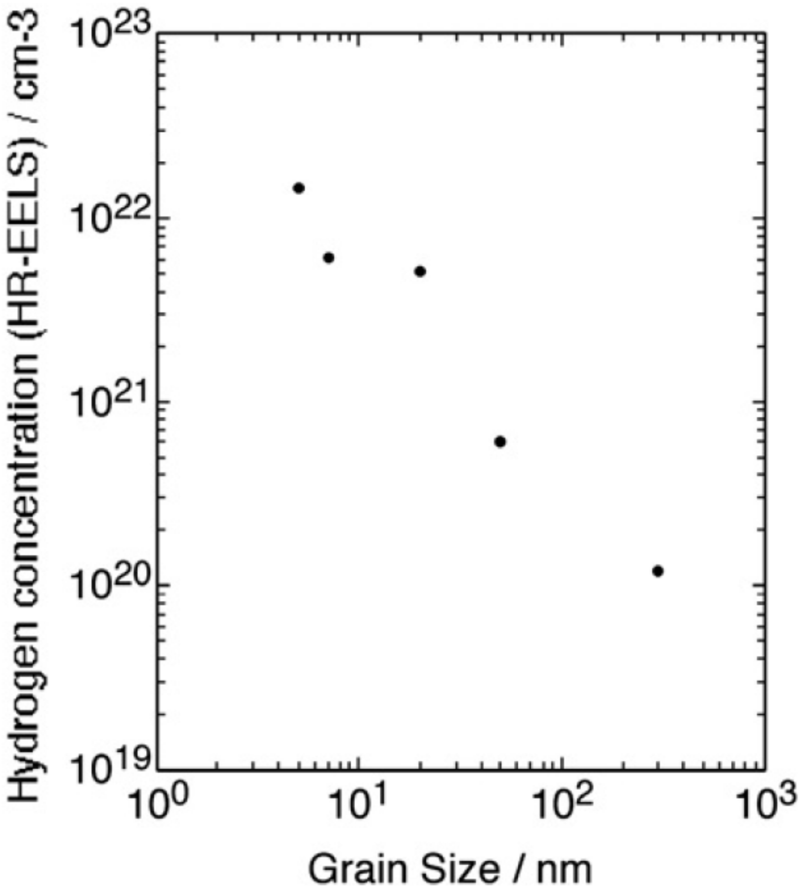

- High resolution electron loss spectroscopy (HREELS): inelastic scattering of electrons near the surface

$\Rightarrow$ Excitation of C-C and C-H vibration modes

$\Rightarrow$ Identification of H bonding: H-sp^2 C and H-sp^3 C

- H concentration calibrated with SIMS

Williams et al. Diamond Relat. Mater. 2008

Optical properties: Raman

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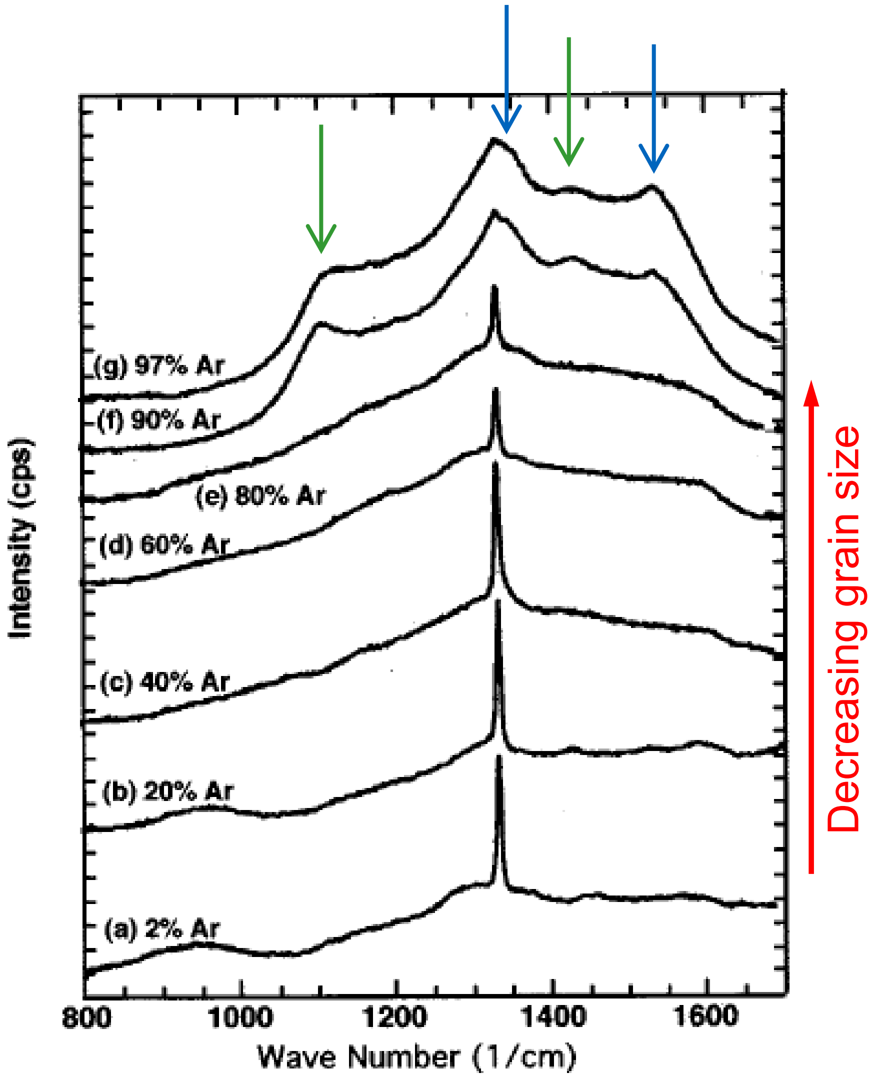

- With decreasing grain size:
  diamond Raman line at 1333cm^{-1} weaker and broadened
- Strong signal of D and G band i.e. sp^2 C
- Diamond peak more pronounced with UV excitation
- New lines at 1140cm^{-1} and 1480cm^{-1}:
  trans-polyacetylene at grain boundaries

Zhou et al. J. Appl. Phys. 1998

Raman: influence of growth parameters

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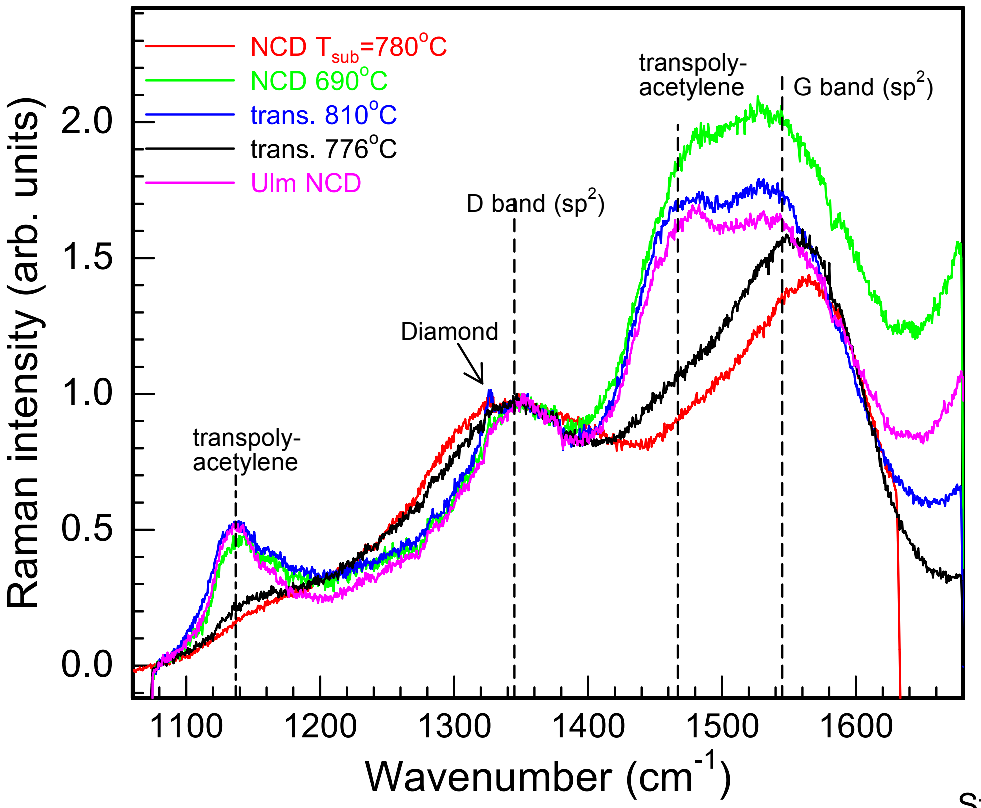

Sternschulte et al. Diamond 2007

- Signal of trans-polyacetylene influenced by growth conditions
- Annealing at 1200°C: trans-polyacetylene lines vanish

Optical absorption UV-VIS

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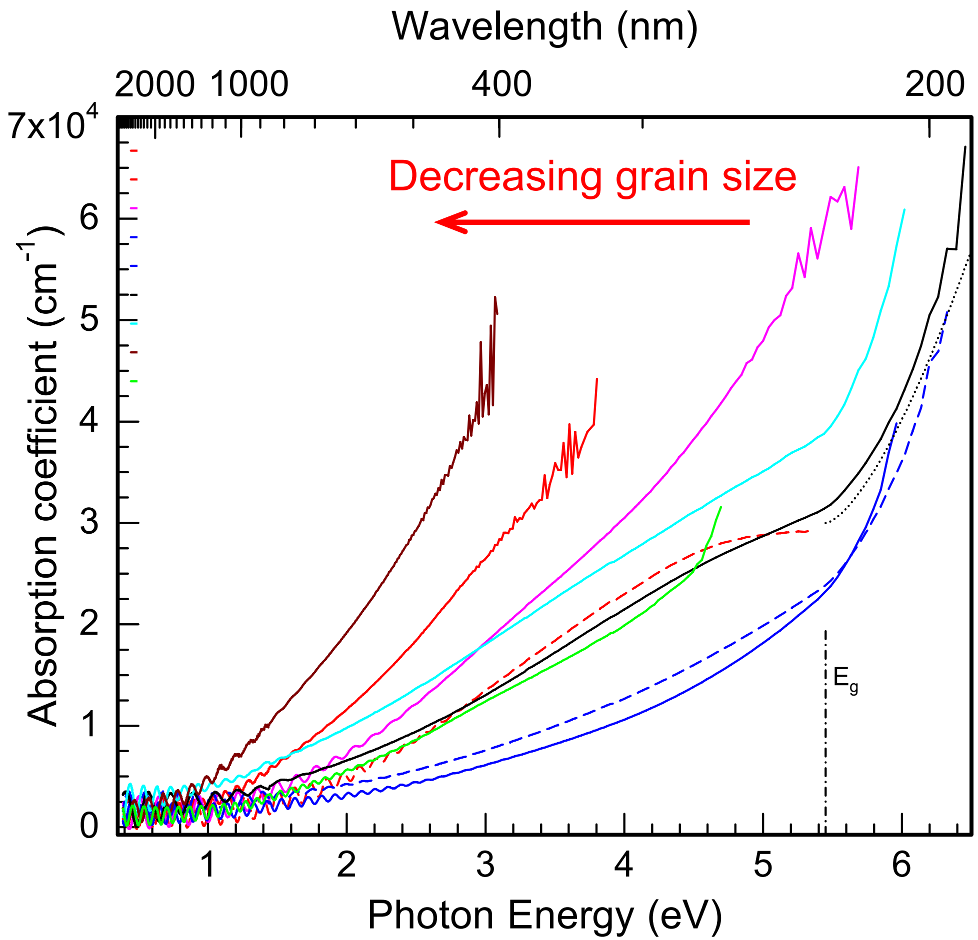

Sternschulte et al. Diamond 2007

- UNCD/NCD: strong absorption in the visible spectral range

UNCD: Optical absorption by matrix

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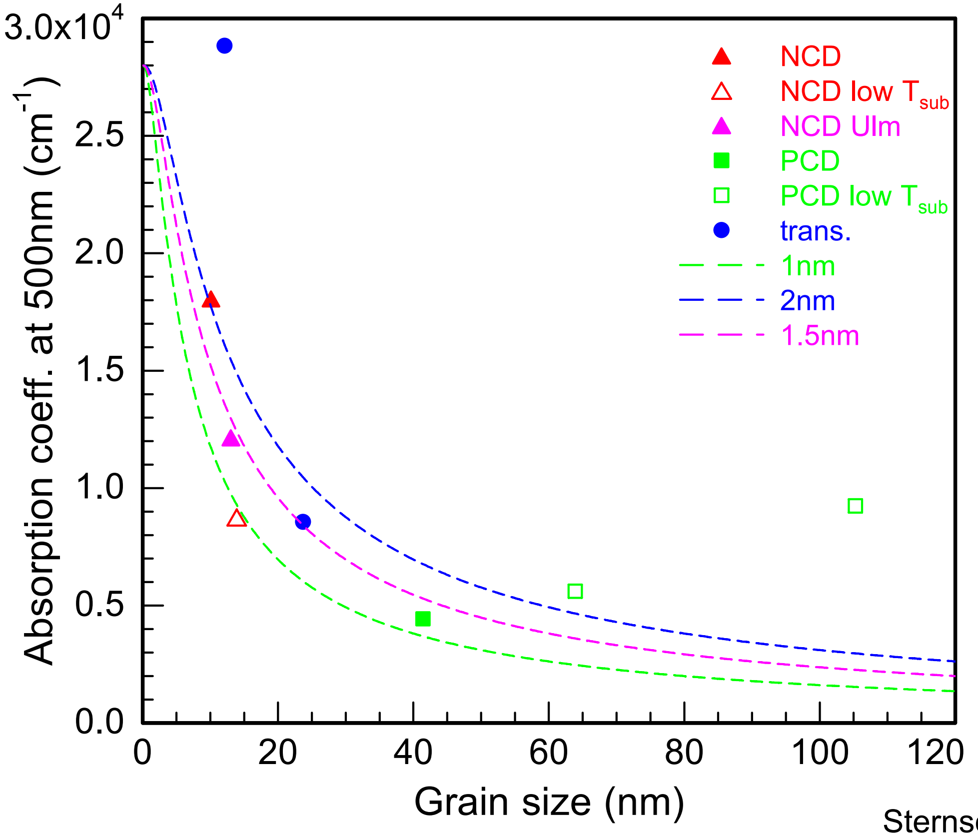

Sternschulte et al. Diamond 2007

- Absorption depends strongly from grain size

$\Rightarrow$ Absorption caused by grain boundary material

Optical properties of UNCD/NCD and “pseudo“ NCD

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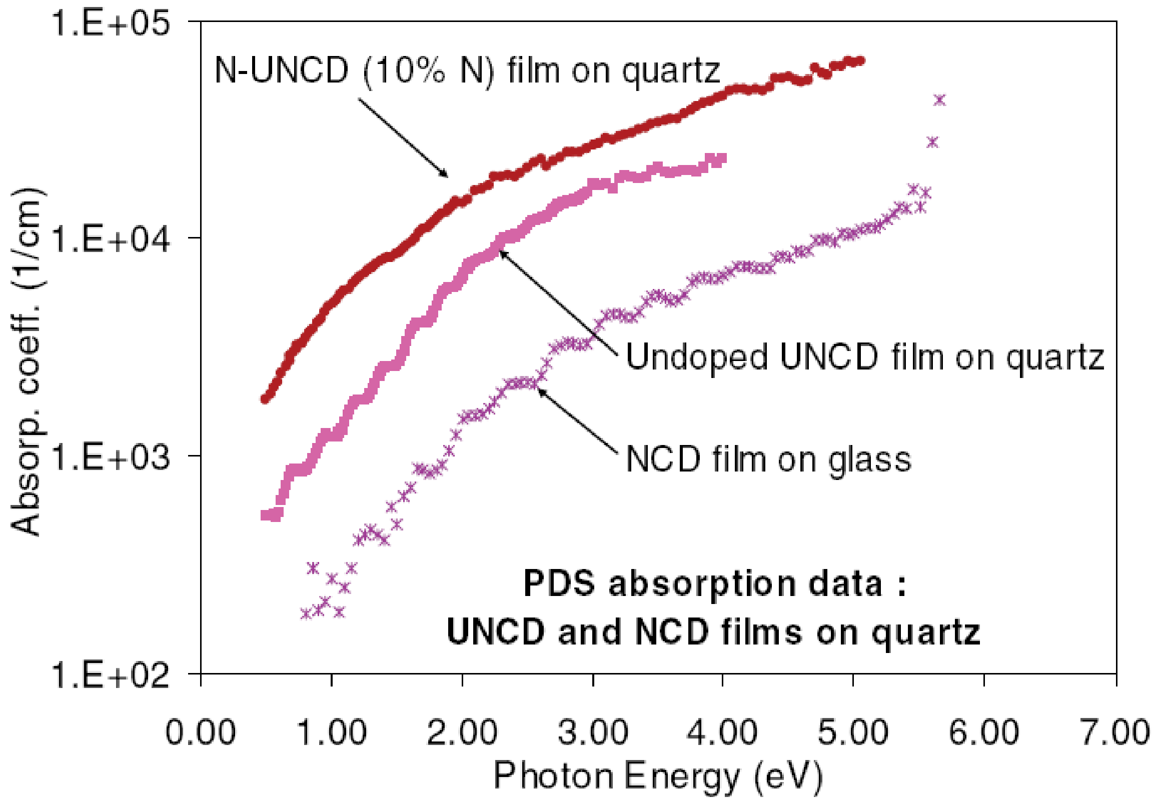

Williams et al. phys. stat. sol. (a) 2006

- “Pseudo” NCD: order of magnitudes lower number of grain boundaries

$\Rightarrow$ Weaker absorption signal

Electronic properties: doping of UNCD/NCD

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- Undoped UNCD/NCD: high electrical resistivity

⇒ Doping required to enhance electrical conductivity

- Doping of diamond

p-type doping:	Boron	E_{AB} = 370meV
n-type doping:	Phosphorus	E_{DP} = 600meV
	Nitrogen	E_{DN} = 1700meV

⇒ Doping of UNCD/NCD with similar approach

UNCD/NCD: p-type doping with boron

- Most literature about boron-doped NCD:
  "pseudo" NCD i.e. growth parameters as PCD

- Influence of boron addition during CVD deposition of UCND?

UNCD deposition without boron addition

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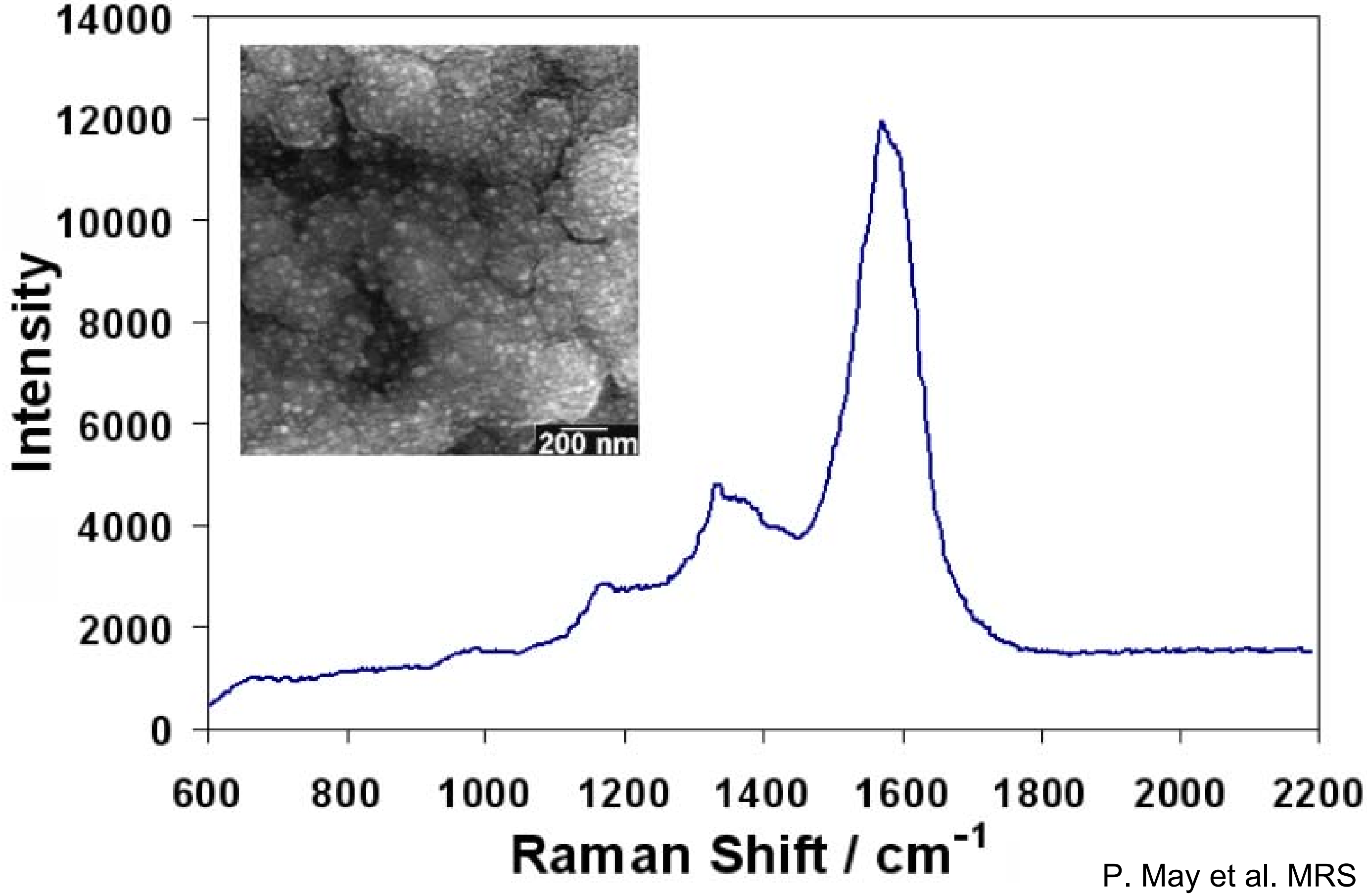

P. May et al. MRS Proc. 956 (2006)

- Deposition of UNCD with hot filament reactor and $CH_4/H_2/Ar$ gas mixture with 0.5sccm CH_4/50sccm H_2/200sccm Ar

UNCD deposition with boron addition

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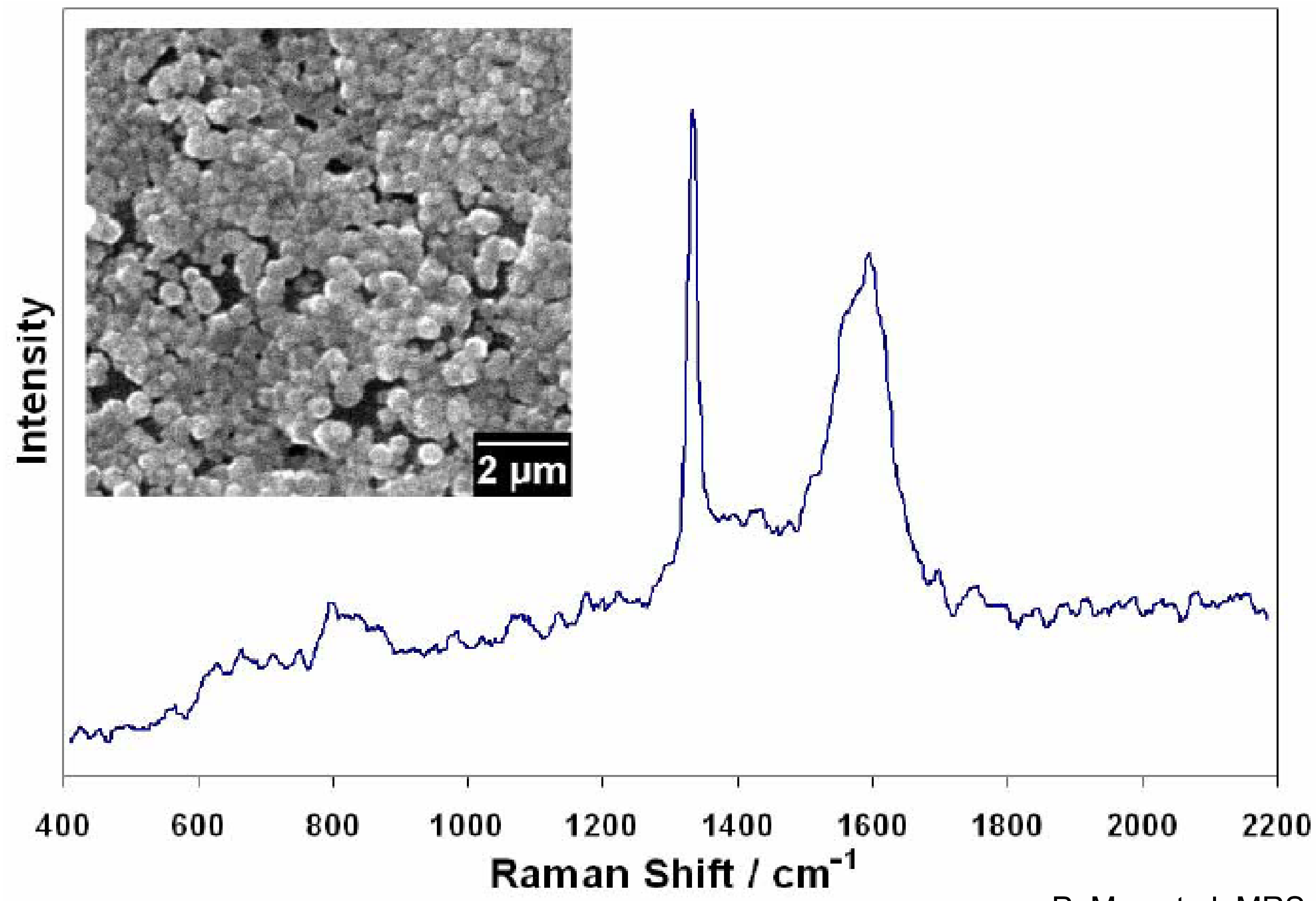

P. May et al. MRS Proc. 956 (2006)

- Addition of B_2H_6 (300ppm with respect to CH_4)

$\Rightarrow$ Change of morphology and growth mode!

Influence of boron addition on UNCD growth

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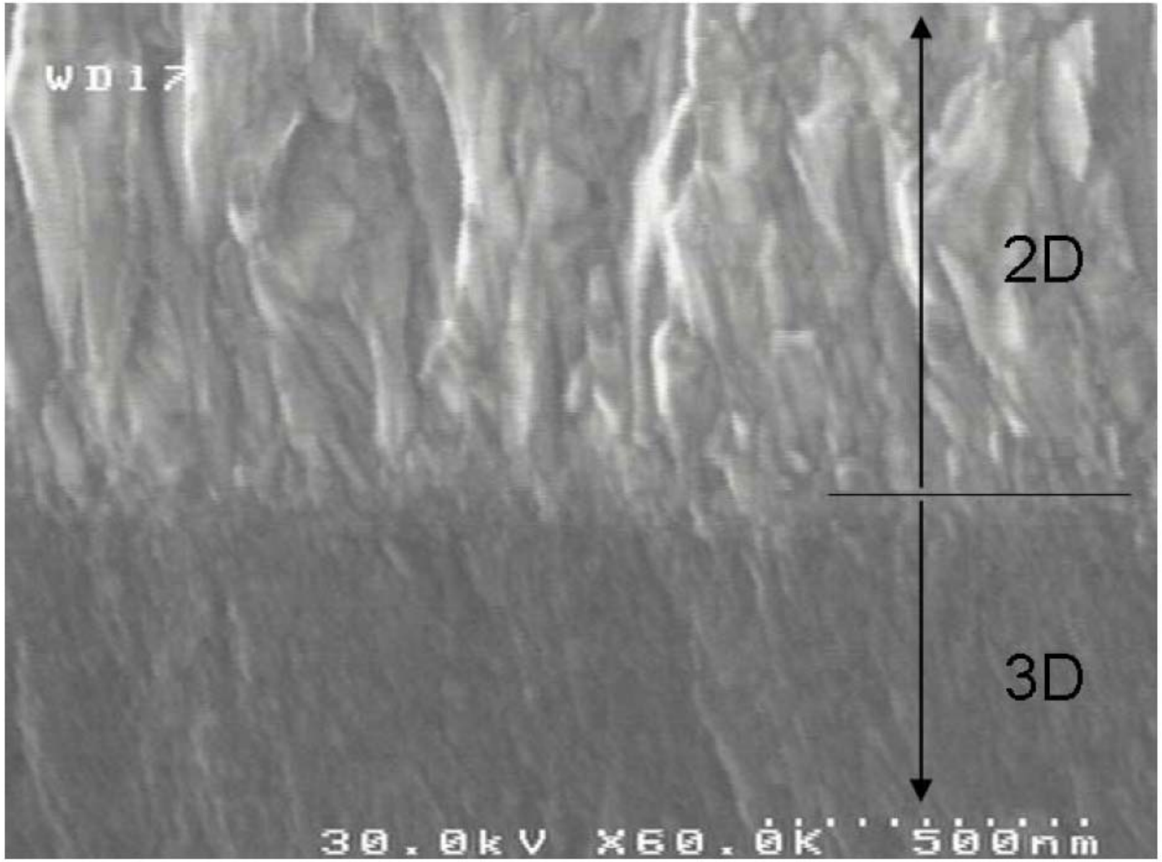


Boron doped layer

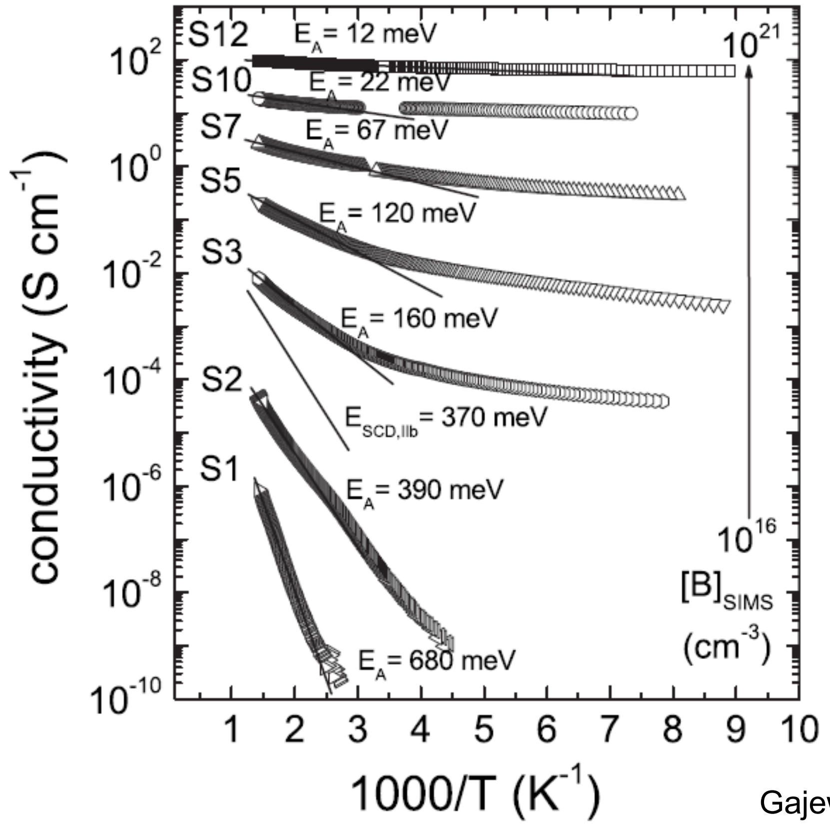
Undoped UNCD

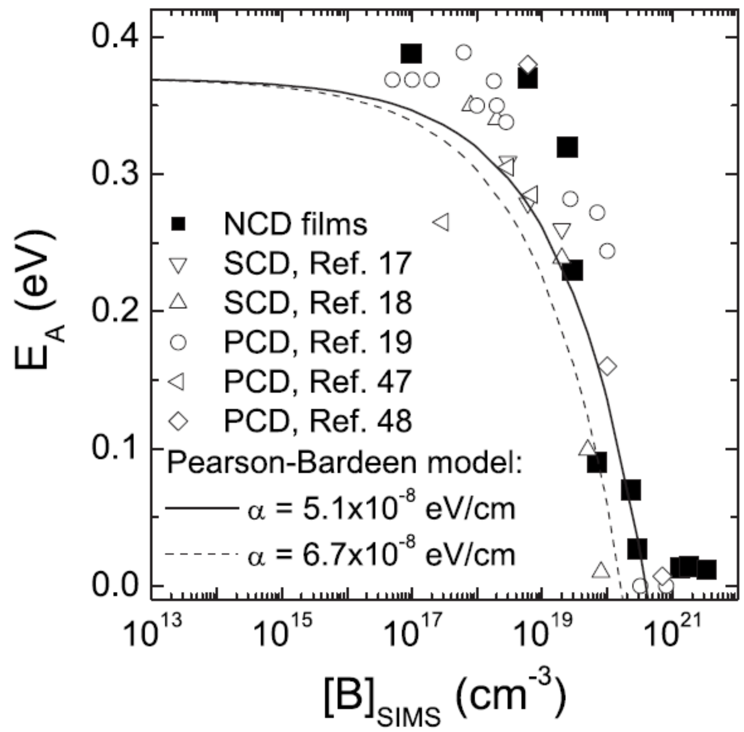
M. Dipalo, Dissertation Uni Ulm 2008

- Reduced secondary nucleation rate

$\Rightarrow$ Change to columnar growth behaviour

Boron doped ”pseudo“ NCD





Gajewksi et al. Phys Rev B 2009

- Doping behaviour comparable to polycrystalline diamond
- Metallic doped “pseudo” NCD:
  superconductive behaviour observable with T_C = 1.7K

Electrical properties of boron doped NCD: influence of grain size

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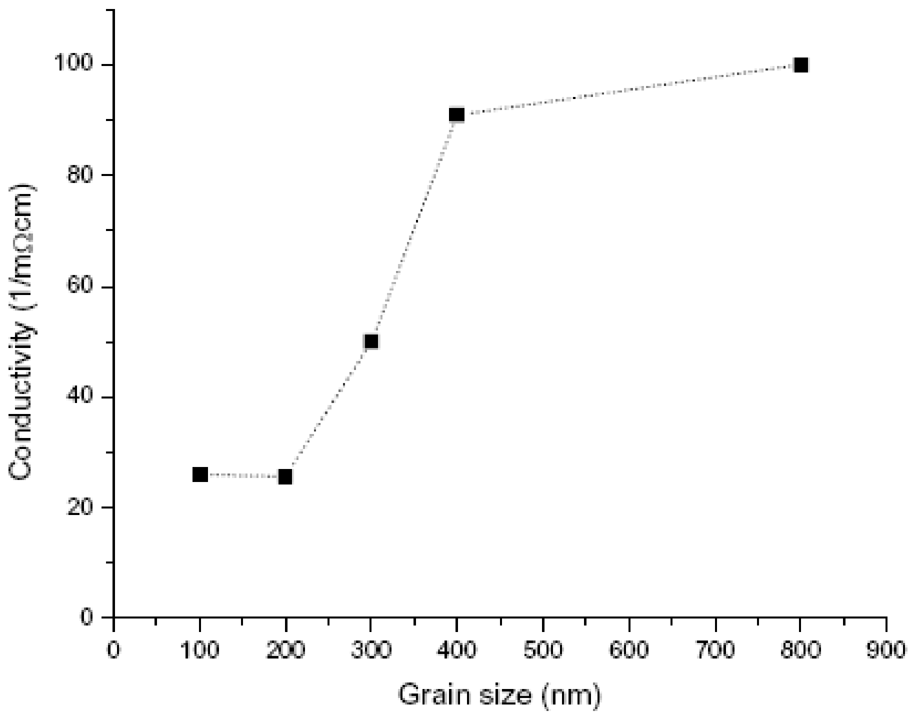

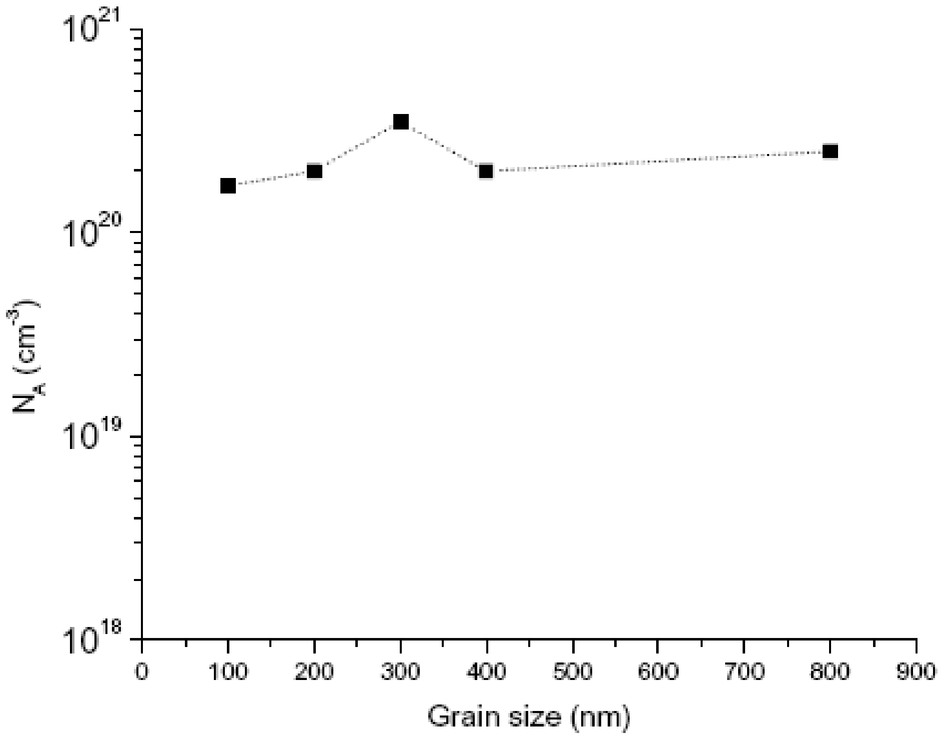

M. Dipalo, PhD thesis, Universität Ulm 2008

- Conductivity is strongly dependent from grain size

Influence of grain size on mobility

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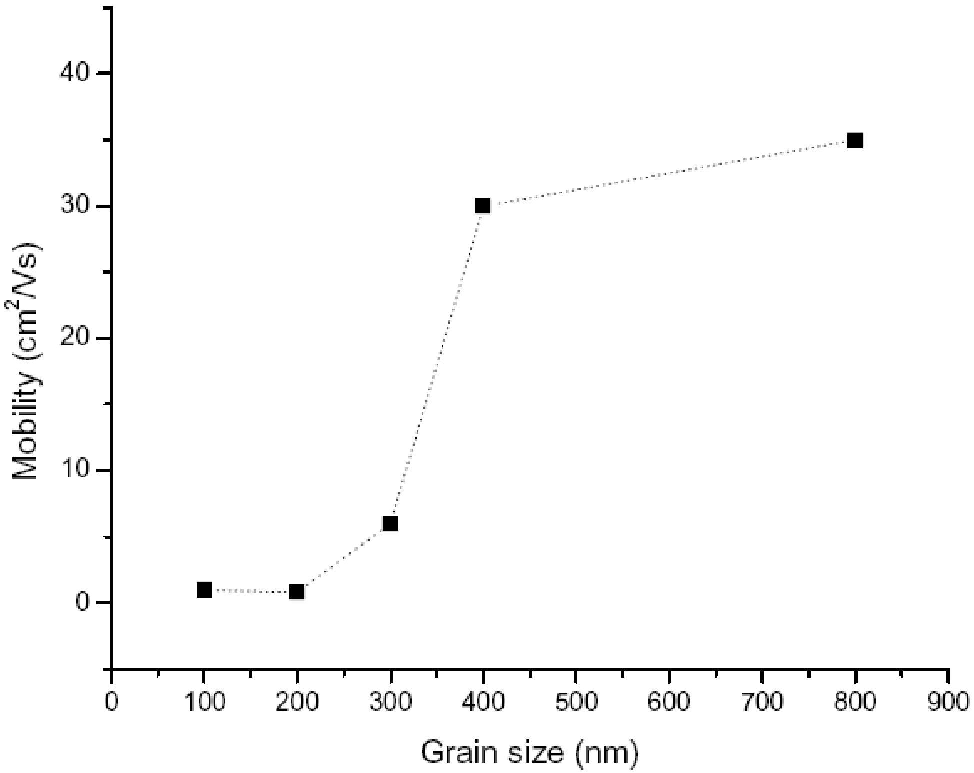
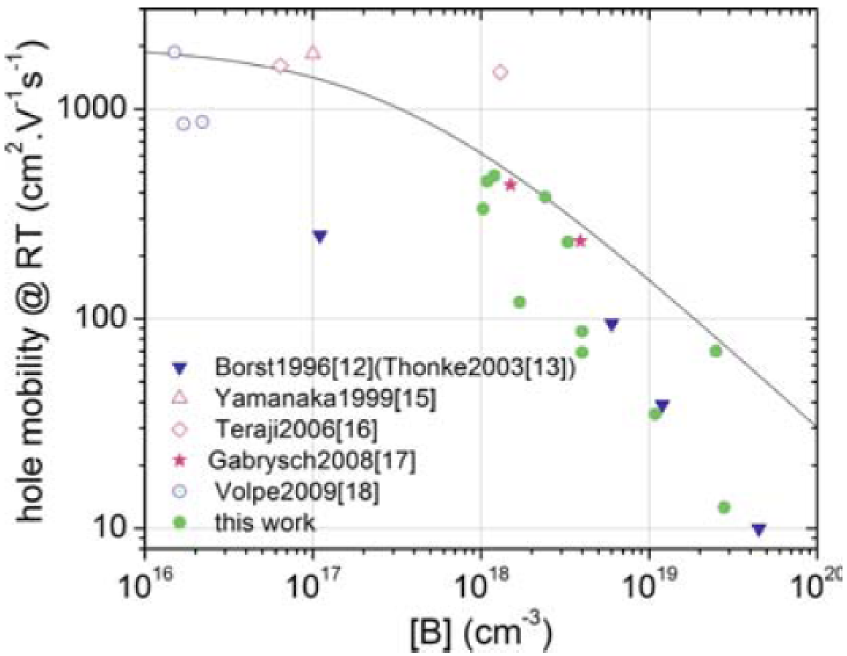


M. Dipalo, PhD thesis, Universität Ulm 2008

Mobility of B-doped monocrystalline diamond



Barjon et al. phys. stat. sol. RRL2009

- Hole mobility drops down with decreasing grain size

n-type doping of UNCD with Nitrogen

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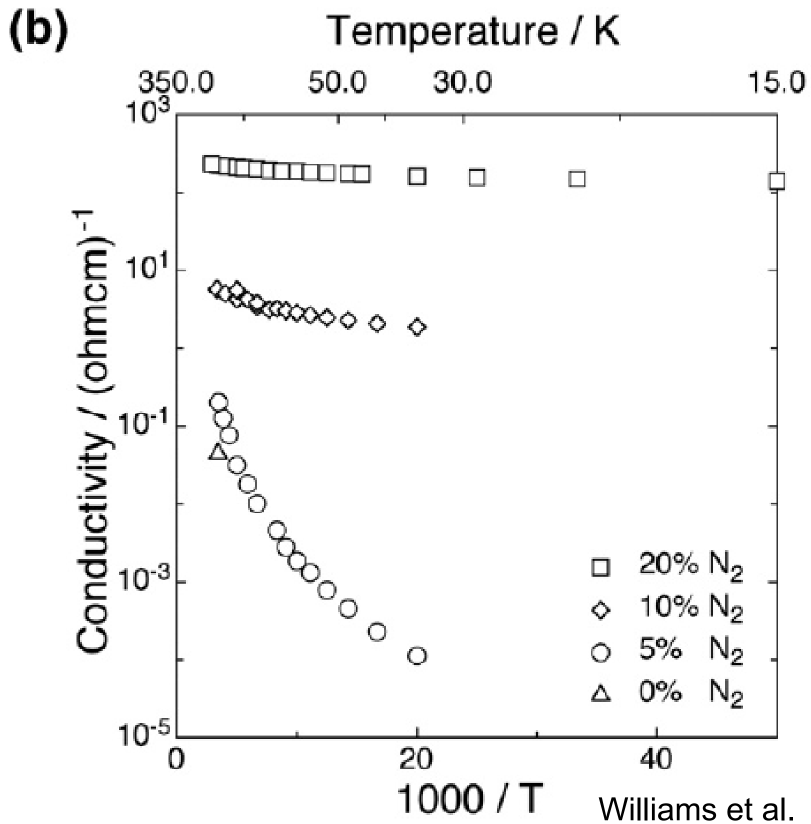
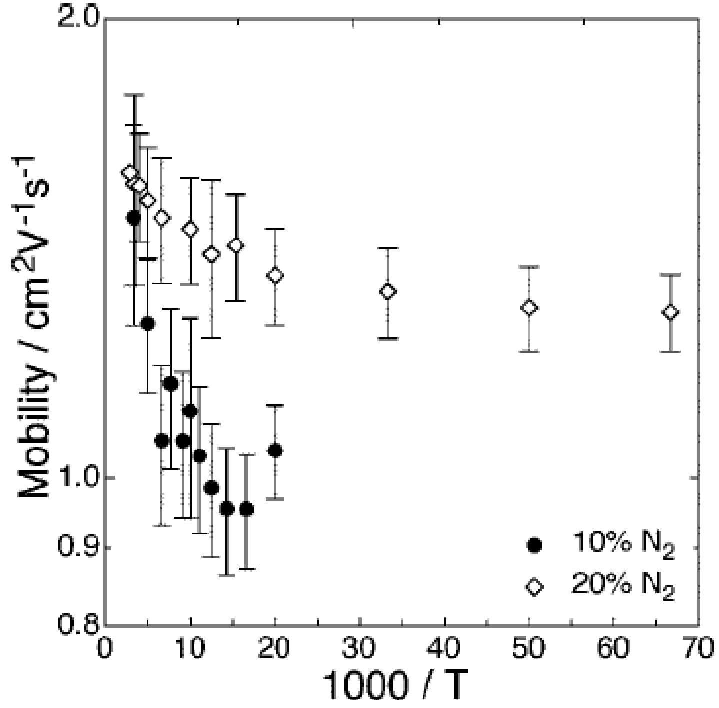


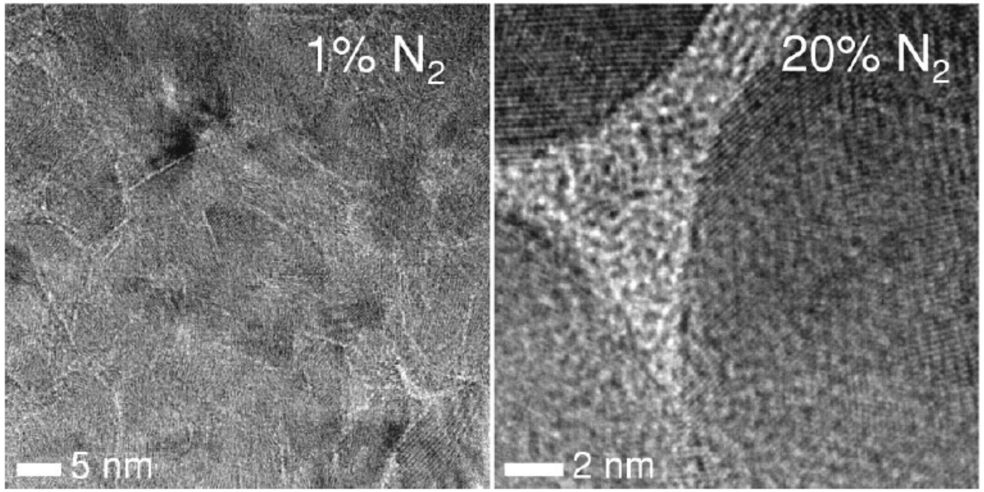
Williams et al.
Diamond Relat. Mater. 2008



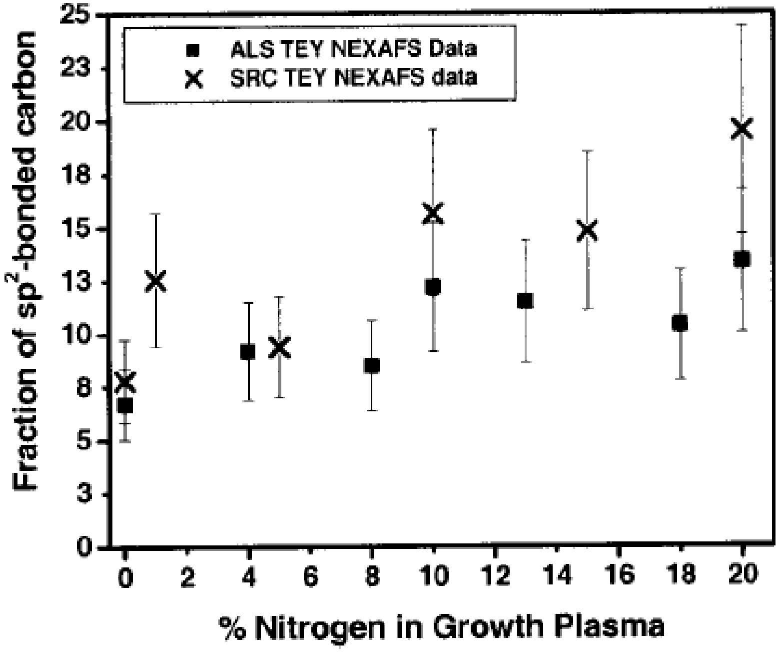
Williams et al.
Appl. Phys. Lett. 2004

- n-type conductivity is observable
- Low activation energies of 10meV

Nitrogen doped UNCD



Bhattacharyya et al. Appl Phys. Lett. 2001



Birrell et al. J. Applied Phys. 2003

- By Nitrogen addition: larger diamond grains
  increased grain boundary width
  slightly increased sp^2 C concentration
- “Grain boundary” doping: modification of the matrix by nitrogen similar to DLC but with much higher mobility

Thermal properties

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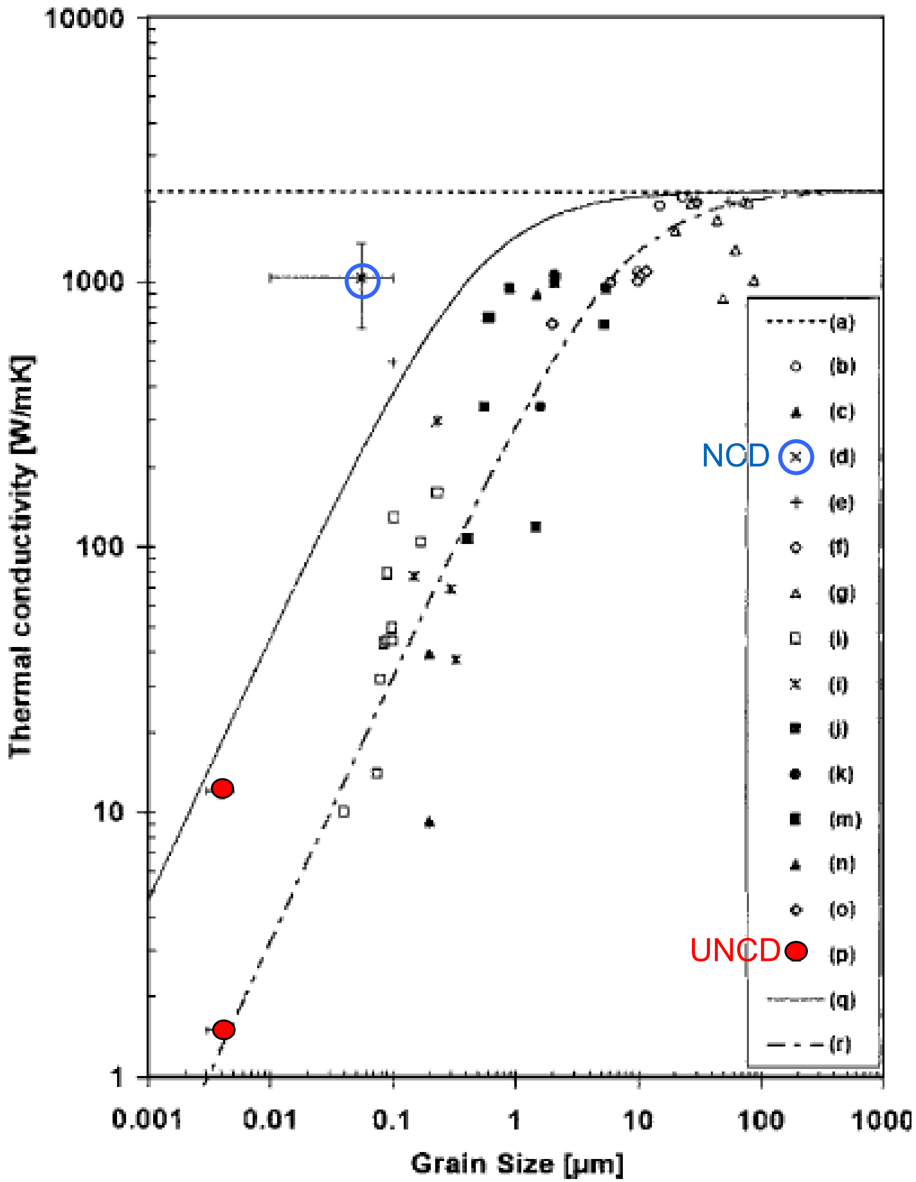

- Thermal conductivity decreases with smaller grain size

⇒ Thermal properties of UNCD rather poor

But: very smooth surface can be advantageous

⇒ Thermal transport of "pseudo" NCD much better

Angadi et al. J. Appl. Phys. 2006

Mechanical properties

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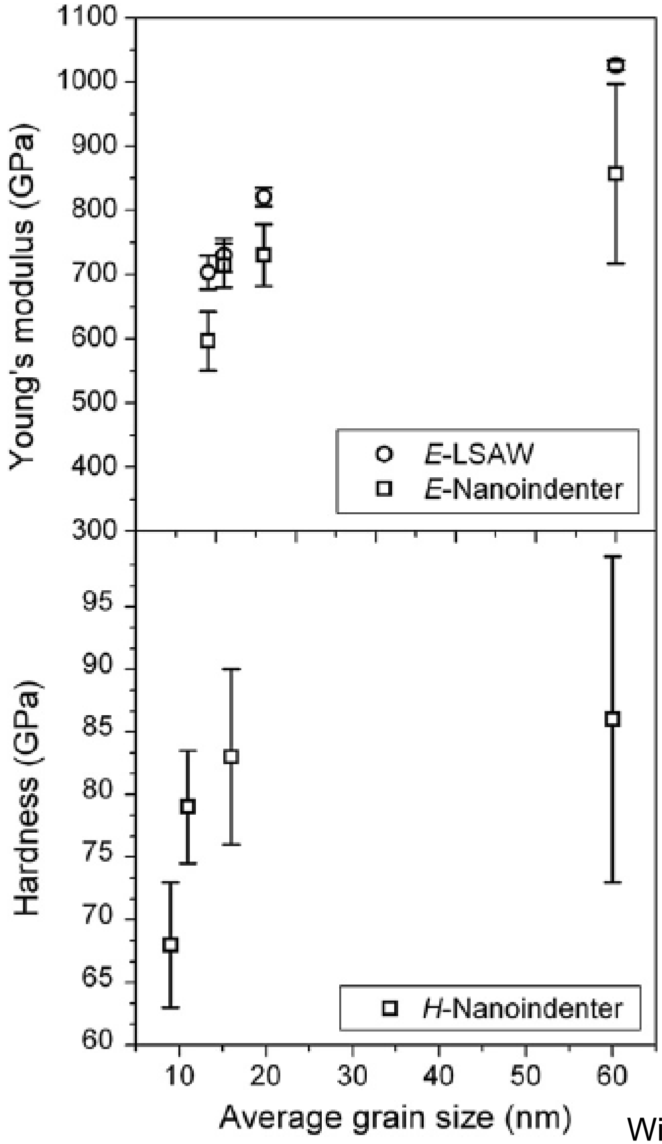

Wiora et al. Diamond Relat. Mater. 2009

- Young modulus depends on grain size
- UNCD with 10nm grains:
  reduction of Young modulus by 30%
- For comparison:
  Si: 130GPa
  SiC: 450GPa

⇒ UNCD ideal for MEMS

Summary

- Ultra nanocrystalline diamond films:
  - very smooth diamond films
  - "homogeneous" isotropic material
- Optical properties dominated by matrix:
  - strong absorption in the visible spectral range
- Electronic properties:

  n-type doping of UNCD by modification of matrix ⇒ n-type possible!

  p-type doping of NCD: comparable to diamond but low mobility
- Mechanical properties:
  - influence of grain size on Young modulus
  - but much higher Young modulus compared to other material

⇒ It depends on the application if UNCD is the material of choice!