Homoepitaxial growth of atomically flat CVD diamond plates in CH_4-rich plasmas

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Outline

- Introduction
  - Motivation
  - Theoretical consideration on the growth mechanism
- Experimental methods
- Experimental results
  - Structural surface characterisation (OM, AFM)
  - Spectroscopic characterisation (Raman, FTIR, CL, PL)
  - Gemmological characterisation (Gran Colorimeter, DiamondView, Cross-Polarized filters)
- Discussion
- Summary
- Acknowledgements

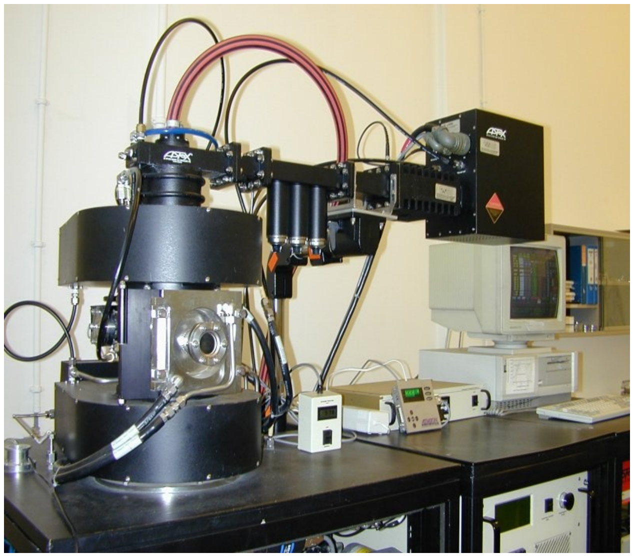
Motivation

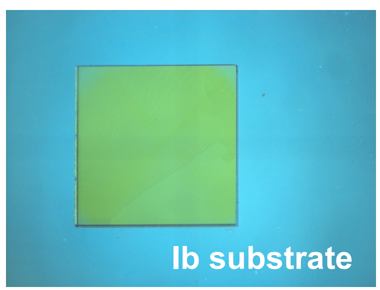
- High quality SCCVD diamond material on HPHT substrates opens up a range of possible applications

- Optics, beam applications, and power electronics
  - very high charge carrier mobilities
  - very long free-carrier recombination lifetimes
  - …

- Synthesis of gem stones
  - stable growth (without formation of non-epitaxial crystallites)
  - thick, optically clear SC diamonds

Setup and conditions



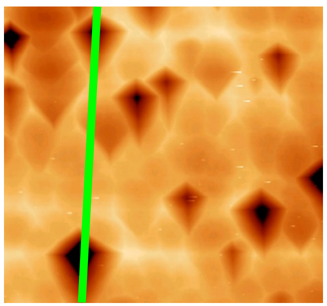


- **Plasma enhanced microwave CVD ASTeX PDS 17 reactor**
- **(100) HPHT Ib diamond substrates (3 x 3 mm² Sumitomo Electric Ltd.) with off-angles in the range 0° - 3°**
- **Wet chemical surface oxidation:** mixture of H_2SO_4 & KNO_3 @ 300 °C for 30 minutes; ultrasonic bath DI H_2O
- **O_2 plasma etching:** 70 Torr, 1000 Watt, 4% O_2 - 96% H_2 @ 800°C, 1 hour
- **Growth:** 180 Torr, 600 Watt, 10-15 % CH_4 - H_2 @ 700°C, > 100 hours
- **Nominally <u>no</u> nitrogen**

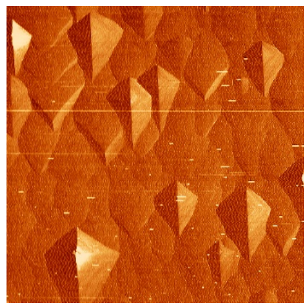
Pre-treated diamond substrate

Scan size = 50 µm R_{rms}= 32 nm

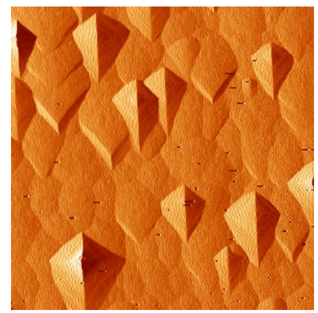
Topography

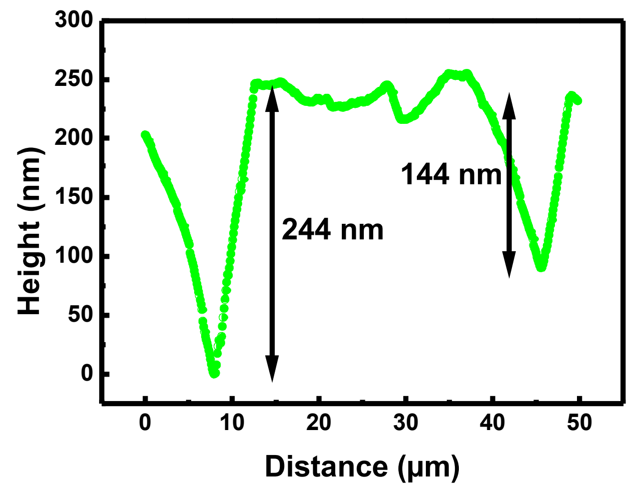


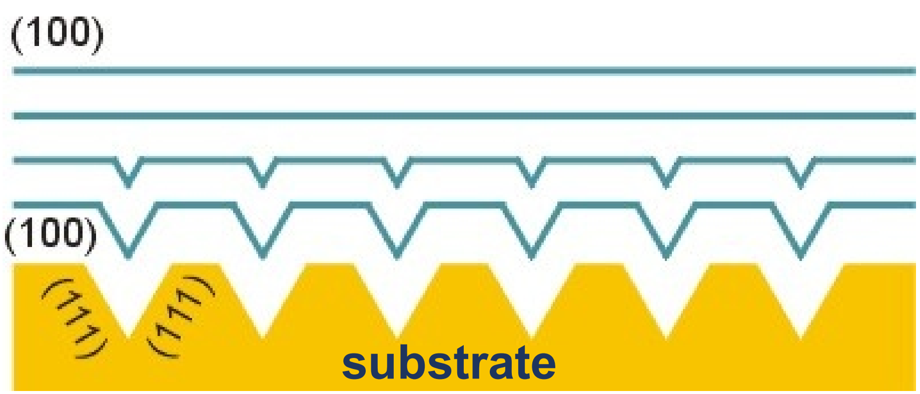
Phase



Amplitude







Smoothening of film surface by van der Drift selection, based on Vollmer-Weber type of growth- (island growth)

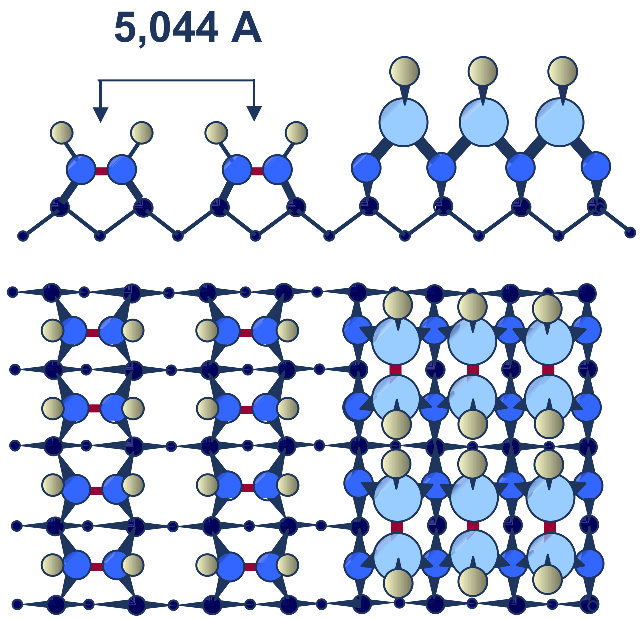
NO STEP FLOW !

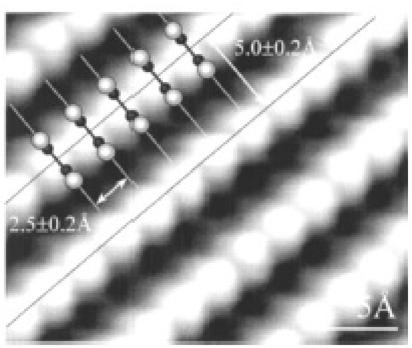
$T_{Debye} > T_{substrate}$

Atomic Structure of H/C(001) Surfaces

Side View

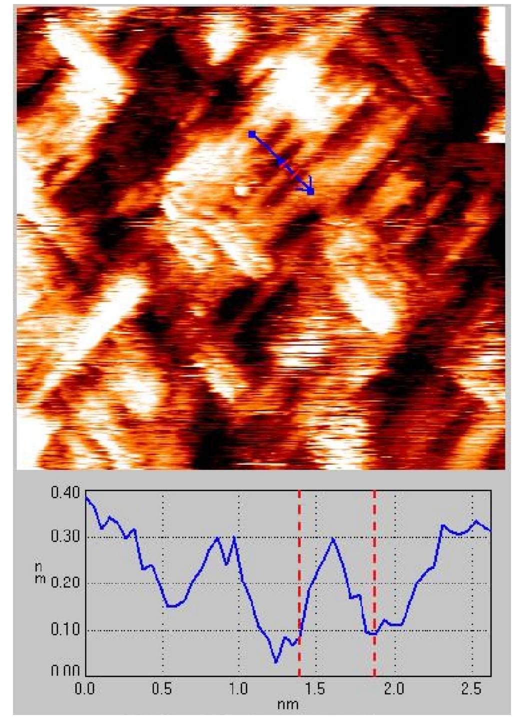
Top View





Bobrov et al. PRB, 2003

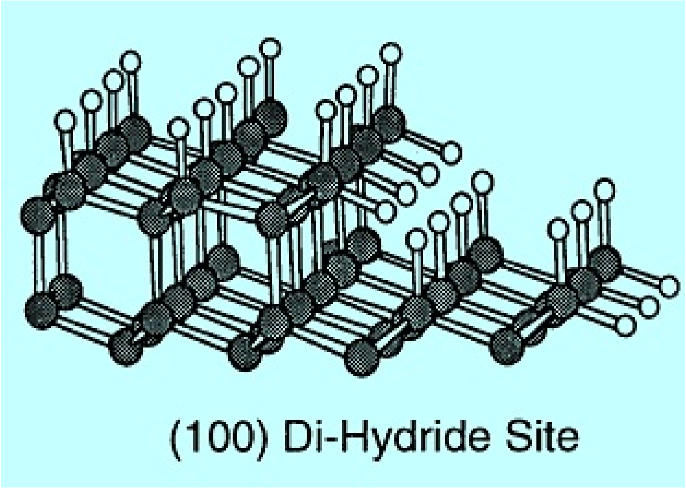
STM after annealing in UHV @ 410°C.

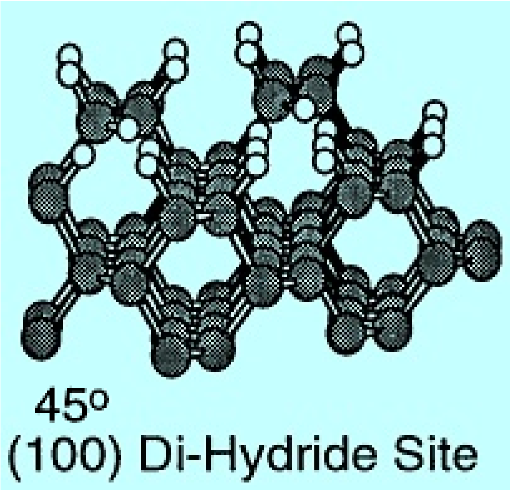


The (2x1) domains are ordered arrays of C-C dimer bonds on different terraces.

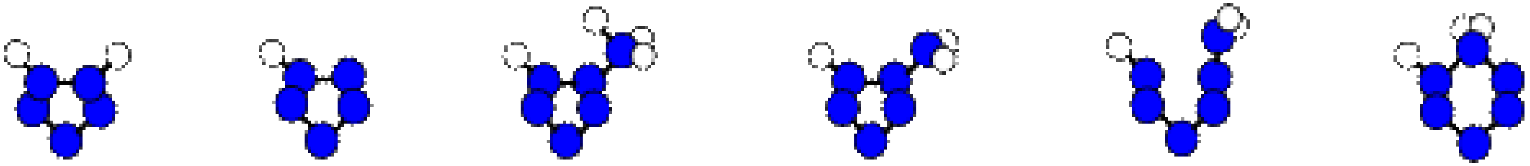
Growth mechanism

- Steps on Diamond (111) and (110) Surfaces



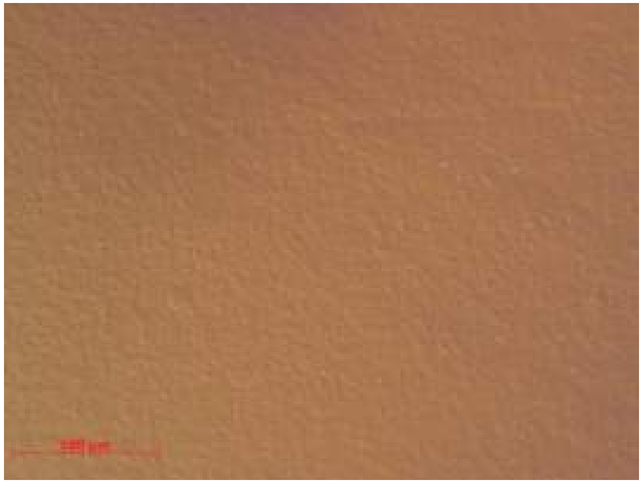


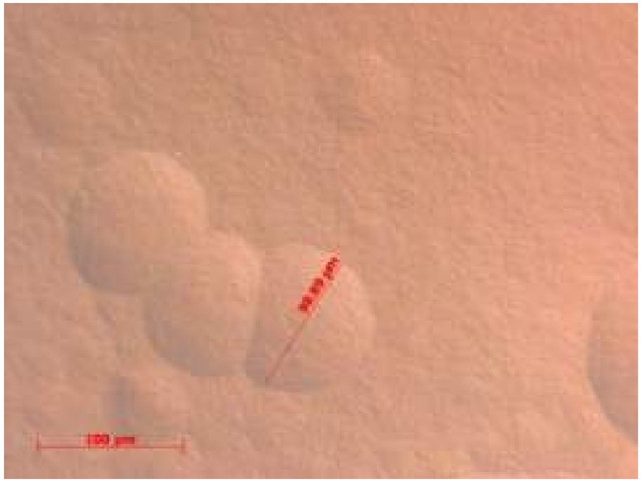
- Layer nucleation on the 100 (2x1) surface requires one C (fastest)



Optical Nomarski contrast imaging

❖ Growth mechanism?

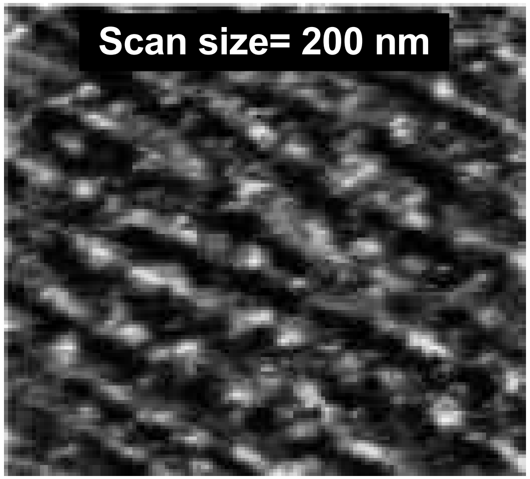




Step-flow mode

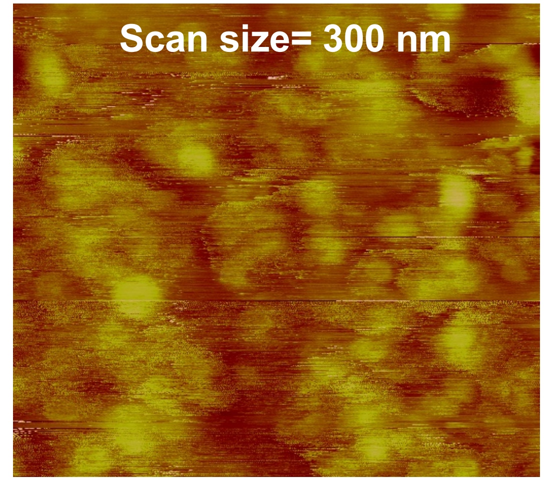
W. Wang *et al.*, Gems & Gemol. V41,N°3 (2005)

AFM morphology



1- 10 µm thick layers

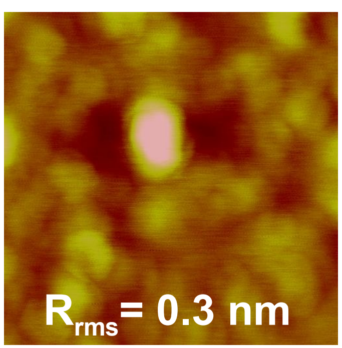
Step-flow mode H.Okushi
Diam. Relat. Mater. 10, 281 (2001)



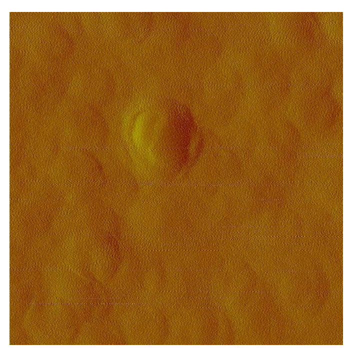
700 µm thick layers

Scan size = 150 nm

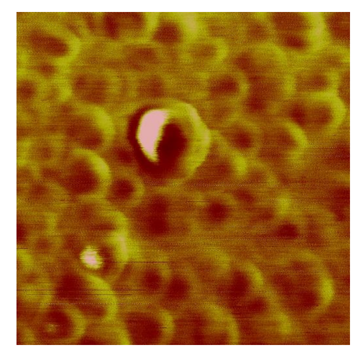
Height



Amplitude



Phase



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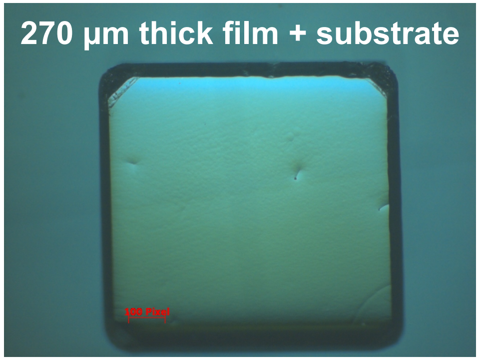
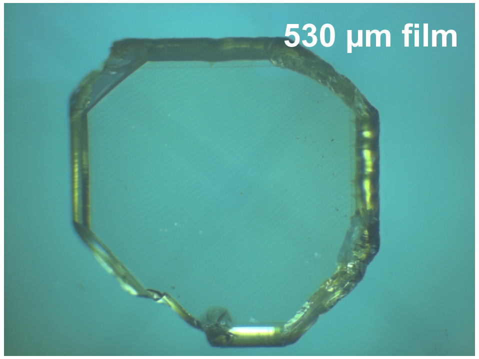
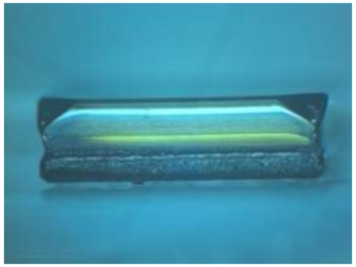
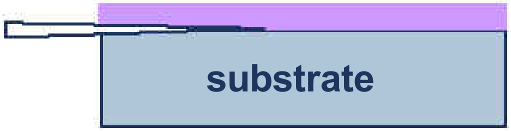
Thick freestanding SC CVD films



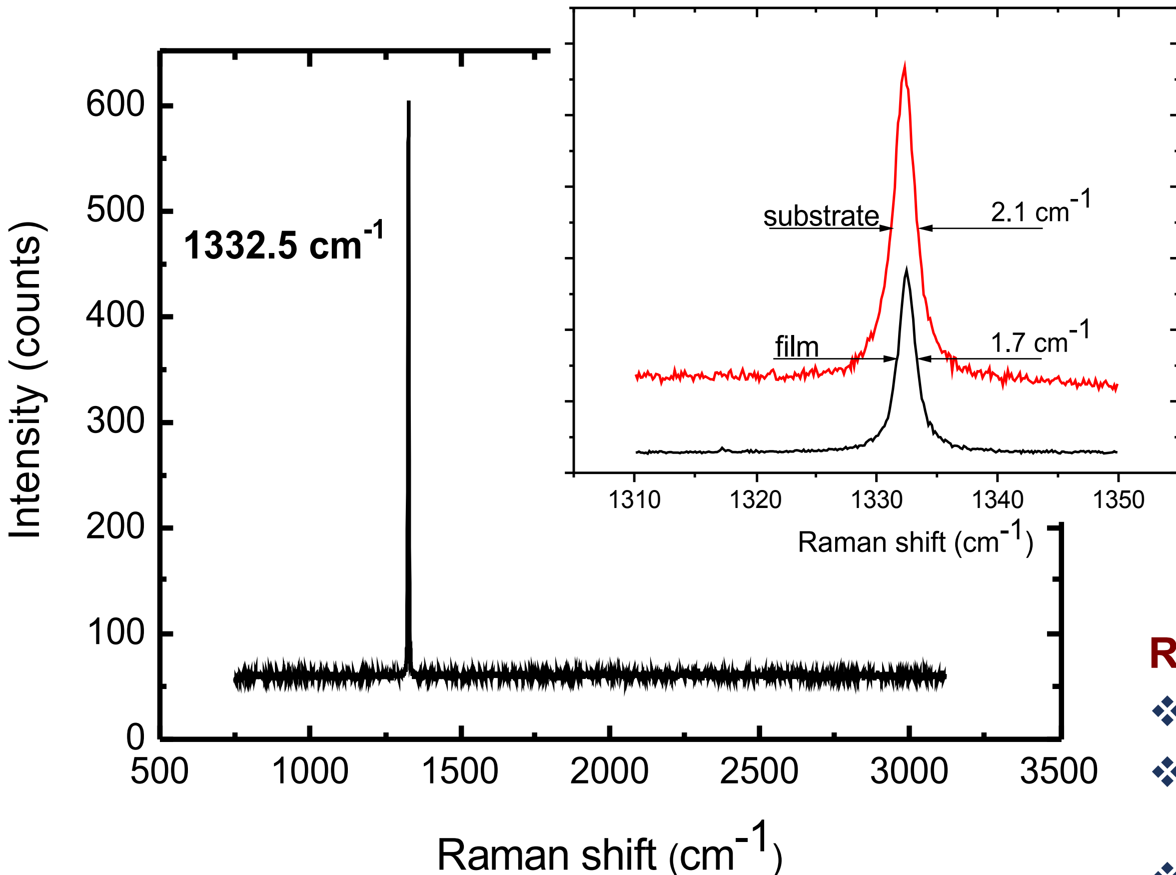






- **Film surface roughness:** R_{rms} **= 0.5 – 1 nm**
- **Growth rate: 7 – 10 µm/h**
- **Laser cutting & polishing (WTOCD, Lier, Belgium)**
- **270 – 1000 µm thick freestanding SC CVD diamond plates**

Raman spectroscopy

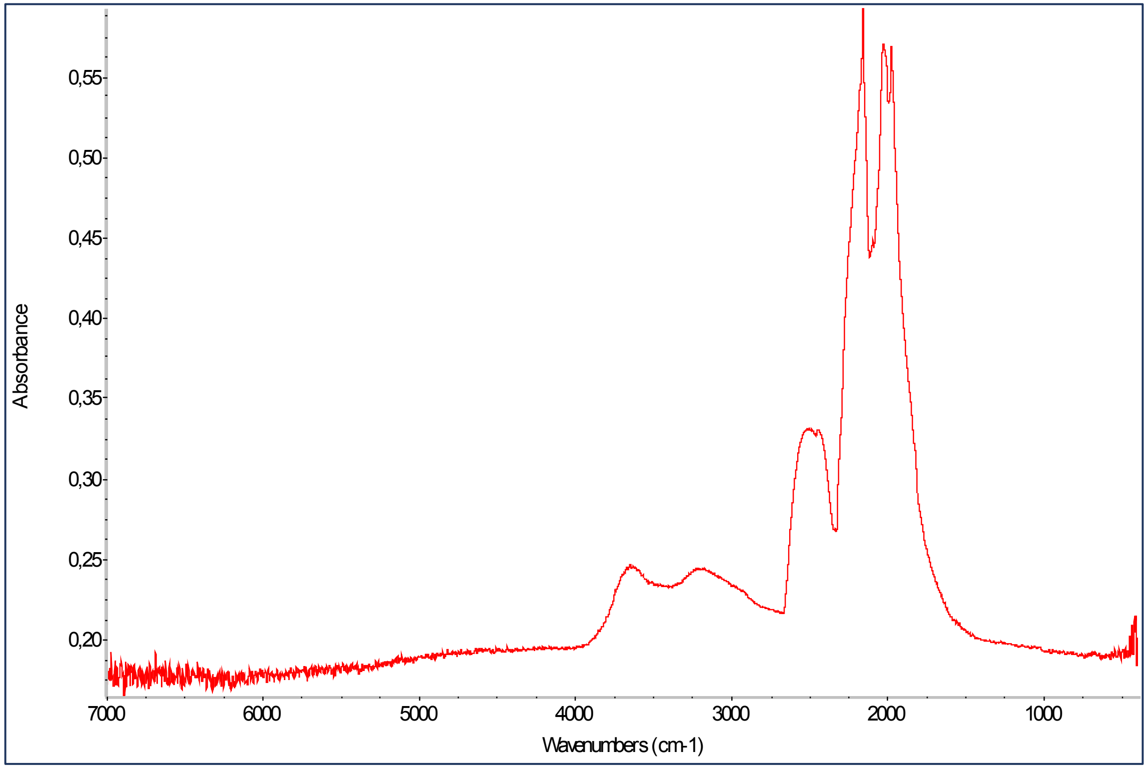


Raman measurements:

- High local crystalline quality
- No existence of non-diamond content
- No stress

J. Maes & V.V. Moshchalkov, Catholic University of Leuven

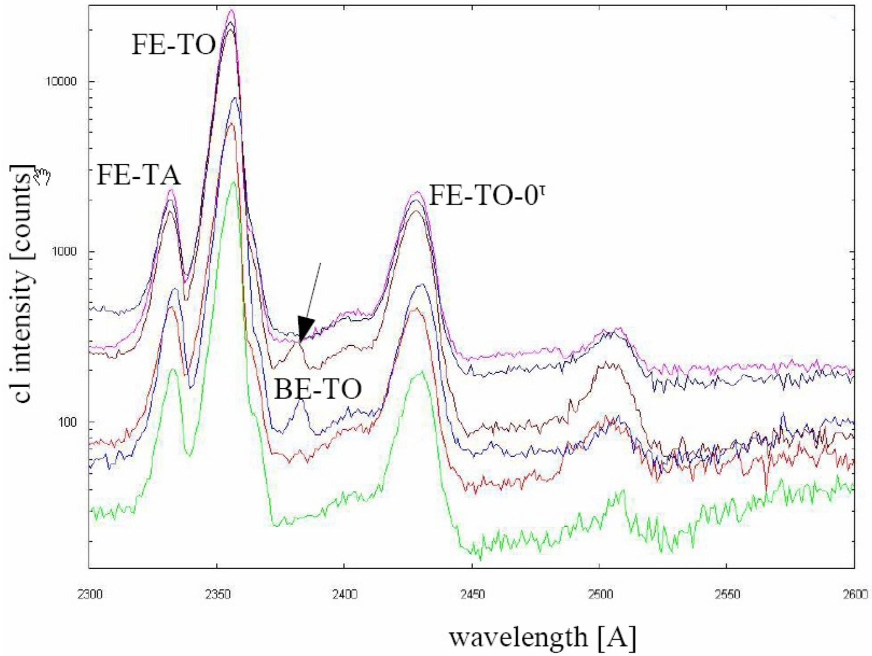
FTIR spectroscopy

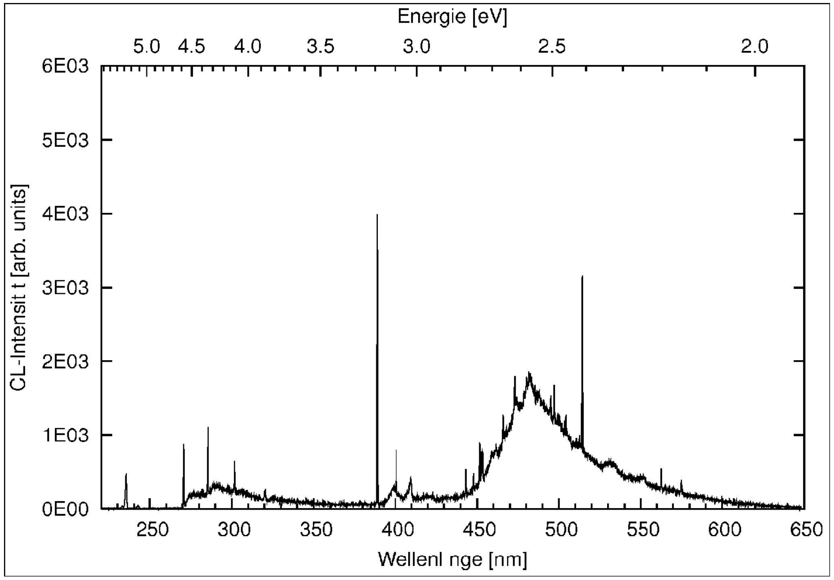


❖ **FTIR measurements:** no impurity related peaks (hydrogen, nitrogen, boron)

→ IIa

CL spectroscopy



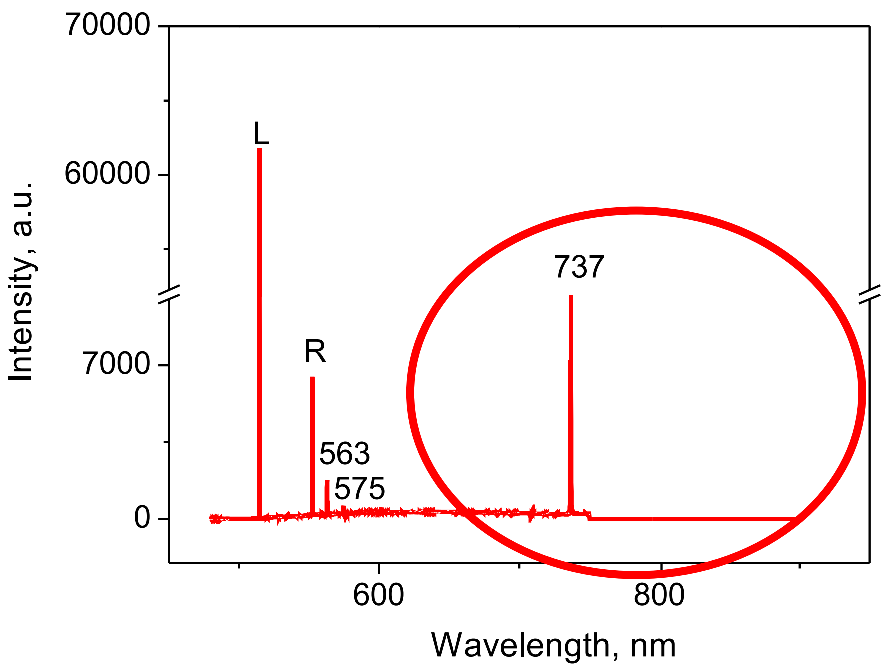


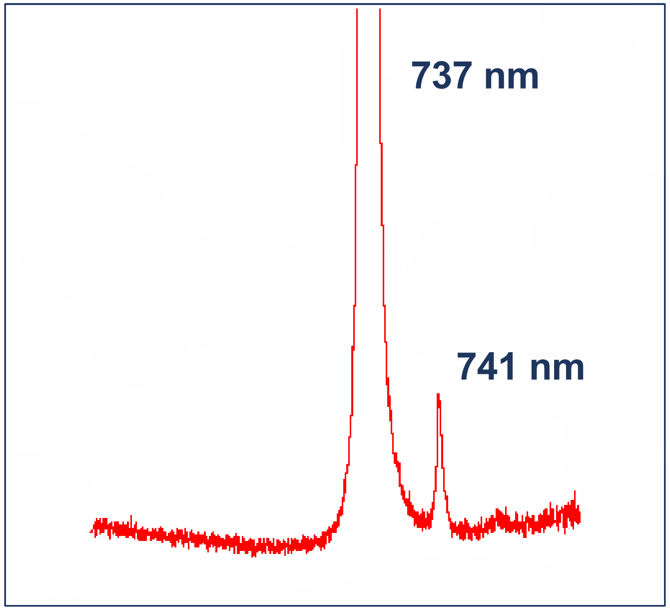
- Free exciton emission
- No bound exciton
- 233 nm – recombination TA
- 235 nm – recombination TO
- Two samples: 3 ppb B
- Others: < 0.6 ppb B

- 480 nm → band-A

P. Geithner & J. Ristein, University of Erlangen-Nürnberg

PL spectroscopy – 514 nm

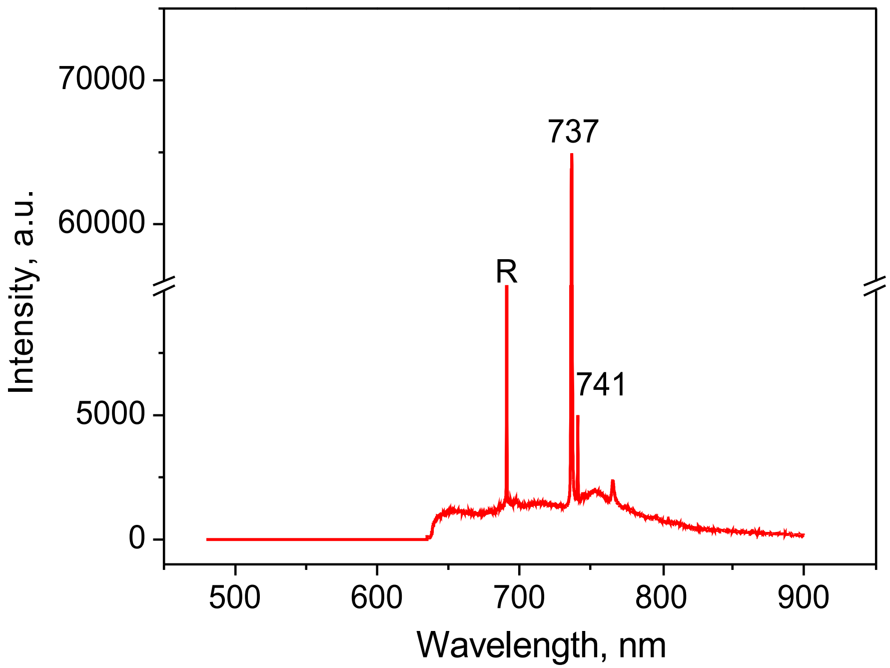


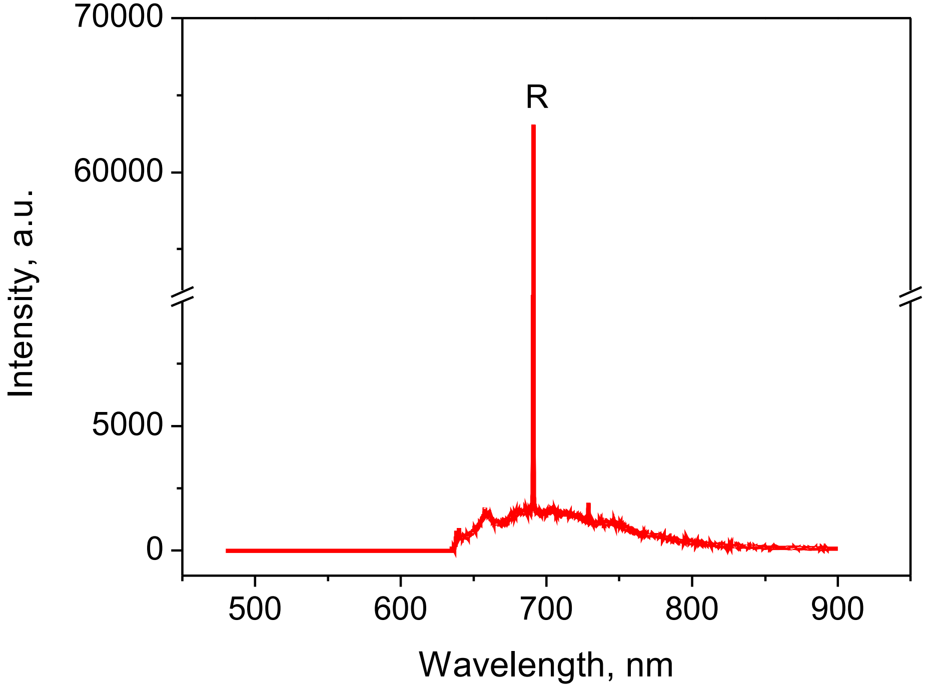


Freestanding CVD films:

- **Weak 741 nm → GR1**
- **Strong 737 nm → [Si-V]**
- **Weak 683 nm → ?**
- **Strong 575 nm → $[N\text{-}V]^{\circ}$**
- **<u>NO</u> 637 nm → $[N\text{-}V]^{-}$**
- **563 nm → ?**
- **Small peaks around 610nm → ?**

PL spectroscopy – 632 nm





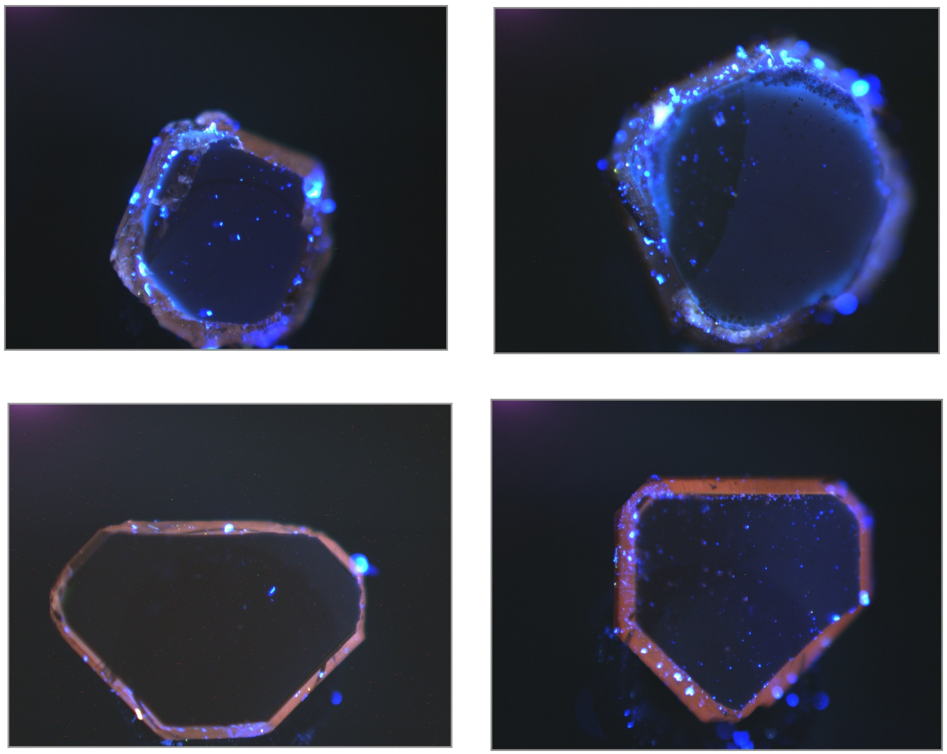
Freestanding CVD films:

- Strong 737nm → [Si-V]
- Weak 741nm → GR1

First CVD films:

- No or weak 737nm → [Si-V]
- No or weak 741nm → GR1

Surface luminescence imaging



SC CVD – DiamondView™:

- ❖ **Blue luminescence → band-A**
- ❖ **Red luminescence → [N-V] centers**

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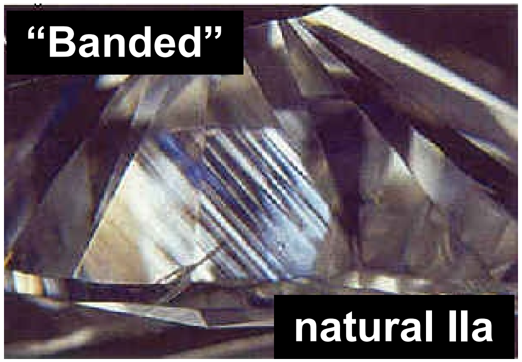
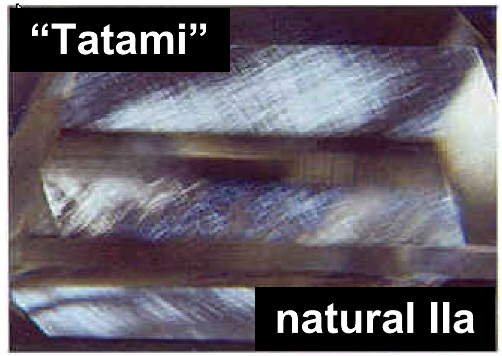
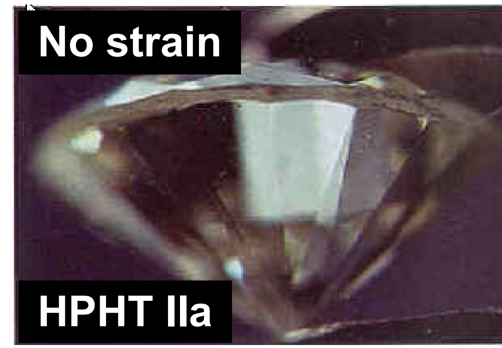
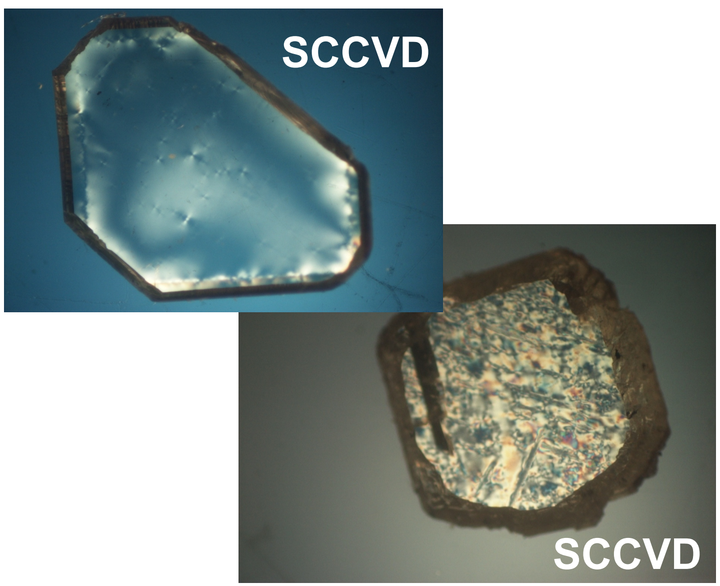
Gemmological microscopy with cross-polarized light



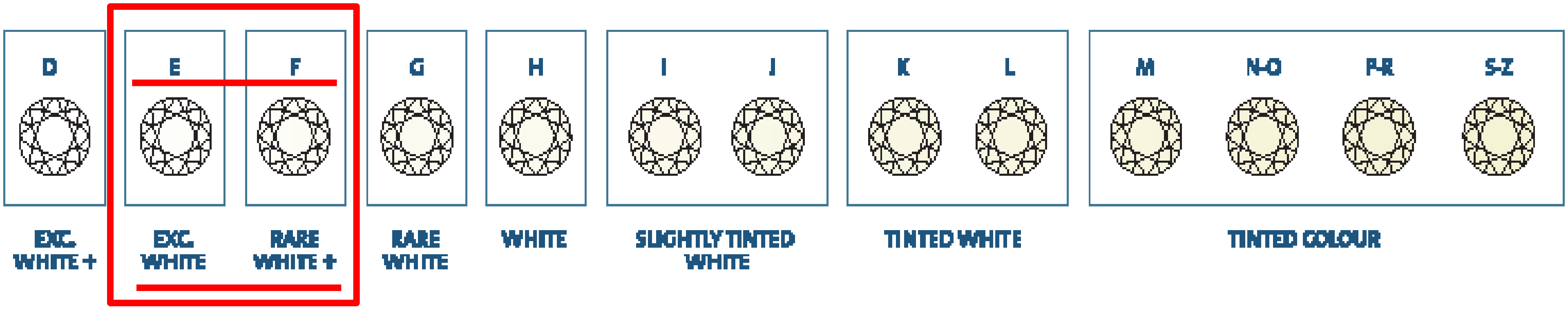




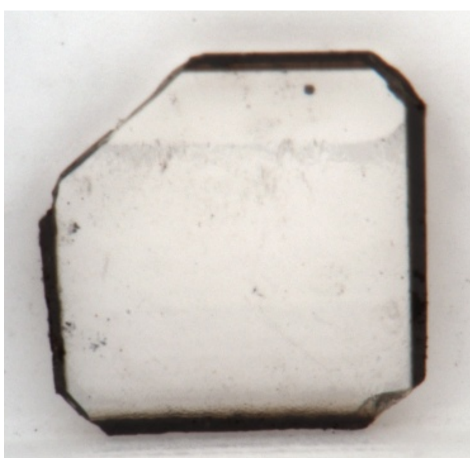
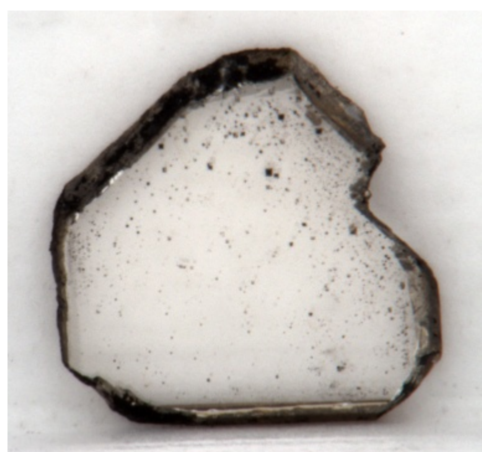
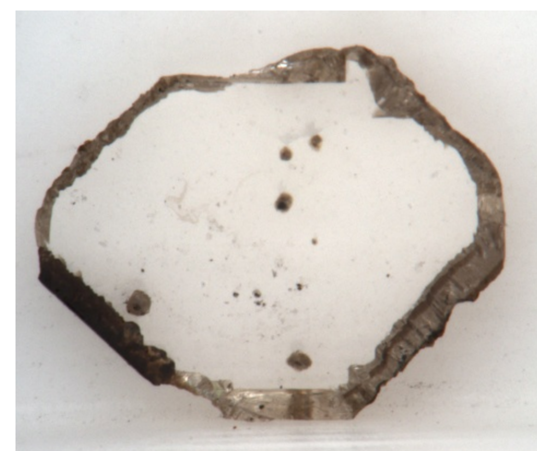


- Residual internal strain → Anomalous birefringence
- **Natural IIa** – "Banded" & "Tatami" patterns strong common features
- **HPHT IIa** – No strain
- **SCCVD** – Crossed-hatched bands of low order interference colors

Diamond grading



10.01.06	08.03.06	20.03.06
0.77 mm	0.84 mm	0.98 mm

Summary

- Thick freestanding high quality homoepitaxial (100) CVD diamond films with near-atomically flat surfaces have been achieved even for films to 1 mm thick.
- High resolution AFM observation has revealed a surface that points to the presence of a different growth mechanism than the well-known step flow growth mode.
- The E - F gemmological colour grade of SCCVD diamond has been achieved.
- FTIR measurements clearly showed all samples to be type IIa material, which nevertheless can be easily distinguished from natural IIa diamond due to the specific internal birefringence features as observed under cross-polarizers under diffuse illumination.
- PL spectroscopy reveals defects such as GR1, unusual for SC CVD diamond.
- CL spectroscopy indicates that the boron content is less than 0.6 ppb.
- Although similar deposition conditions were used for the samples discussed here, the defect-related luminescence and colour can differ noticeably.

Acknowledgements

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