High growth rate homoepitaxial diamond deposition on off-axis substrates for detector applications

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Outline

- Motivation
- Growth on on-axis substrates
- Growth on off-axis substrates
- Structural characterisation
  - high resolution x-ray diffraction (HRXRD)
  - μ-Raman
  - photoluminescence
  - chemical purity (N, B)
- Detector properties
- Summary

Motivation

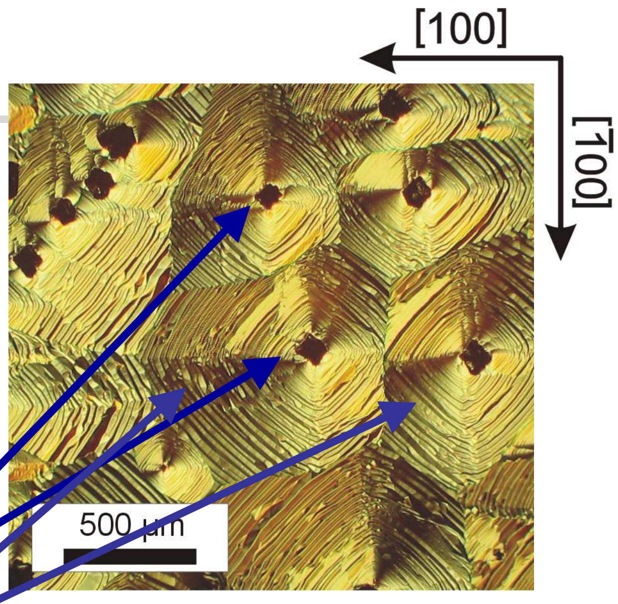
- high quality CVD diamond films on HPHT substrates feasible
  - very high charge carrier mobilities (e.g. $\mu_{electron}$=4500 cm^2/Vs, Isberg et al.)
  - strong excitonic recombination at room temperature (Watanabe et al.)
- high growth rate
  - moderate cost of CVD diamond
  - avoiding of nitrogen (deteriation of electronic properties)
  - stable growth (without forming of non-epitaxial crystallites)

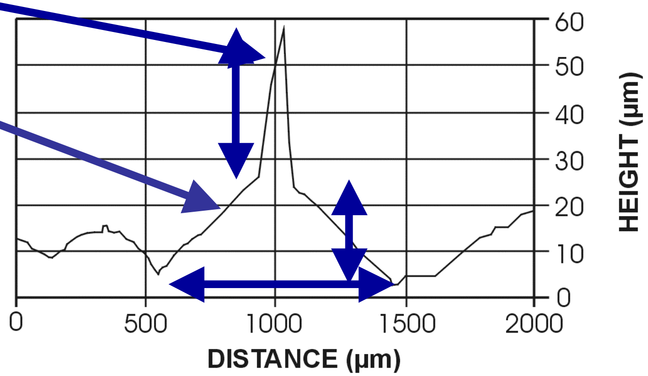
General growth conditions

- substrates:
  - (001)-oriented Ib-HPHT diamond (nominally on-axis or 3-8° off-axis towards [100])
  - containing 10-100 ppm nitrogen
- process parameters:
  - $T_{substrate} \approx 1200$ °C
  - p=130-<u>200</u> mbar
  - $P_{microwave}$=1400 W
  - <u>5</u>-20% CH_4 concentration in H_2 ,for some samples up to 2% CO_2
  - nominally **no** nitrogen
- growth rate: 6-30 µm/h
- film thickness: 100-1300 µm

Growth on on-axis substrates I: pyramidal hillocks/non-epitaxial diamond

- sample:
  - 100 µm thick
  - growth rate: 6 µm/h
- forming of pyramidal hillocks (PH)
  - height ≈ 20 µm, width ≈ 1000 µm
  - inclination ≈ 3° towards [110]
  - non-epitaxial crystallites on top
  - side faces **free** of non-epitaxial crystallites, step bunching
- non-epitaxial crystallites (NC)
  - height ≈ 30 µm
  - growth rate higher than surrounding epitaxial diamond

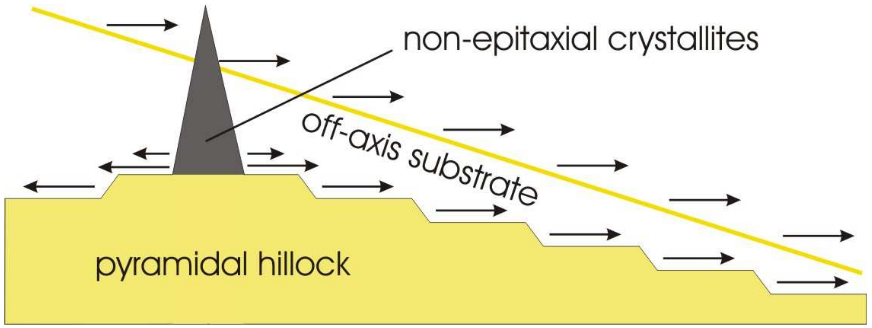




Growth on on-axis substrates II: formation of pyramidal hillocks

- How do PHs develop?
  1. formation of non-epitaxial crystallites
  2. NCs are nucleation centers for new lattice planes
  3. lateral spread of the lattice planes
  4. macro-steps due to step bunching
- Why are **no NCs on side-faces** of pyramidal hillocks?
  - growth by lateral step flow mechanism
  - steps of side-faces sources of new lattice planes

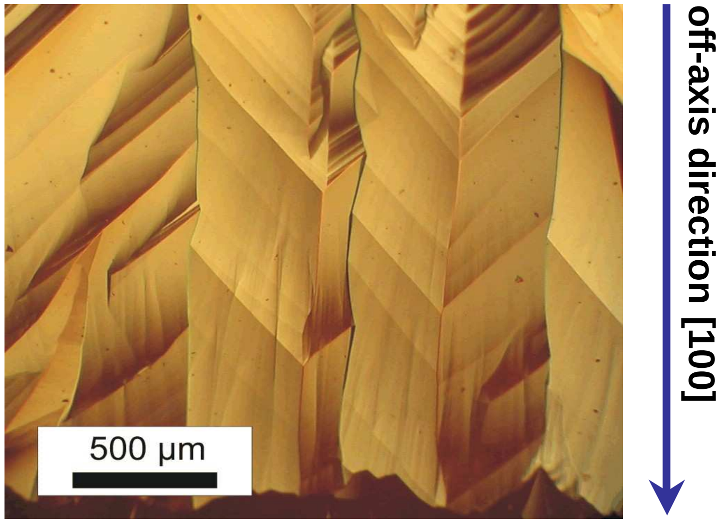
    ⇒ suppression of NCs by lateral overgrowth



Idea: reproduce conditions on side-faces by using off-axis substrates

Growth on off-axis substrates I

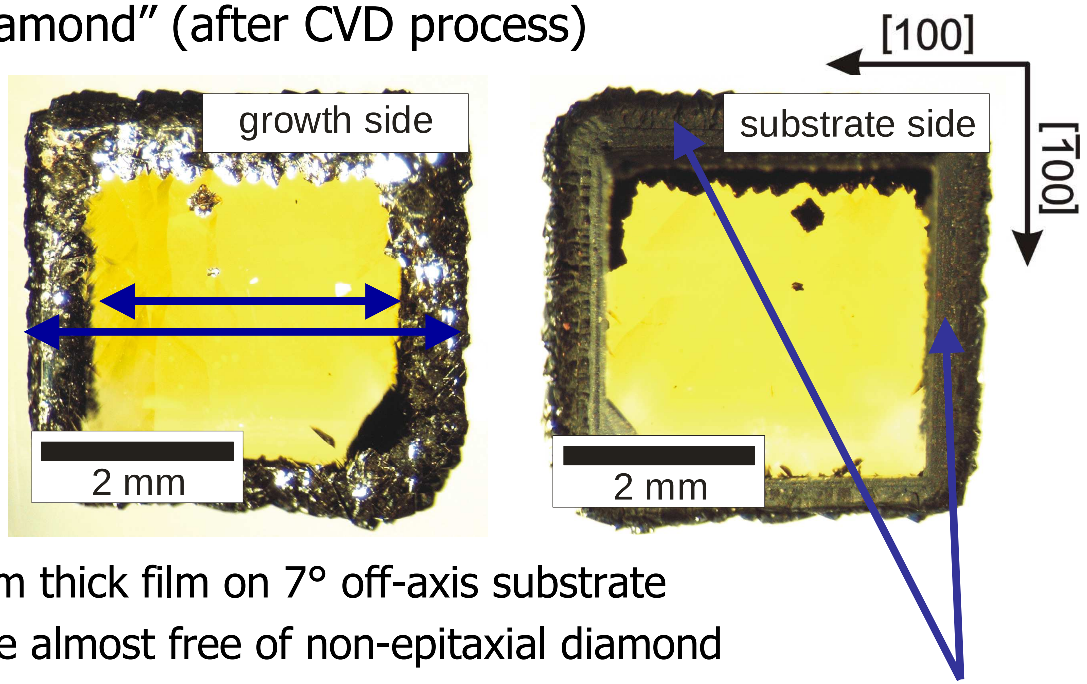
- Idea works



- **Complete suppression of NCs and PHs**

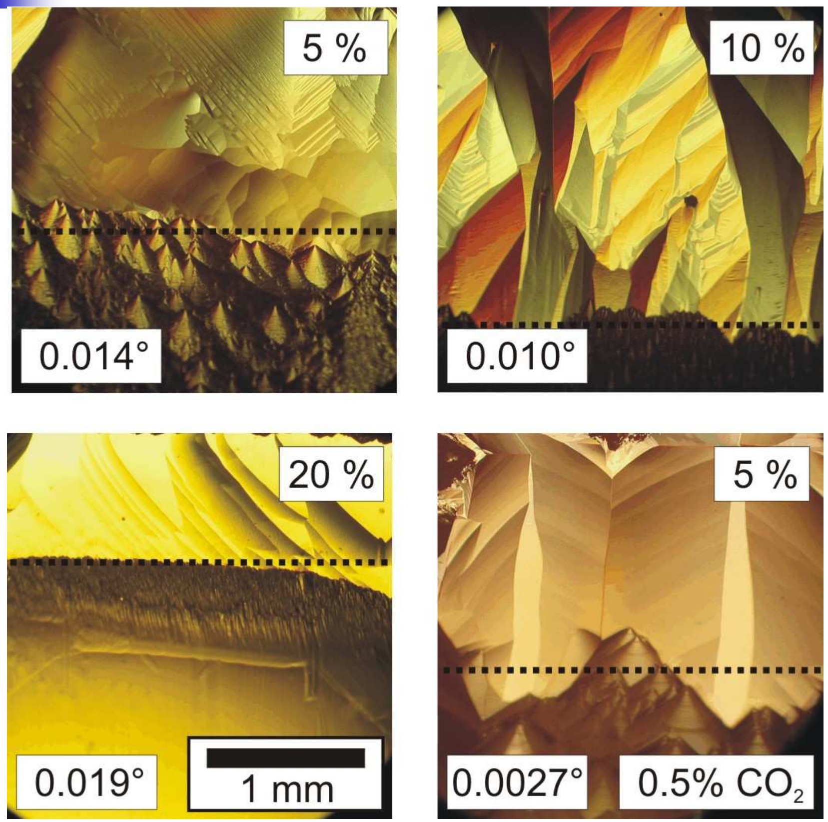
Growth on off-axis substrates II

- "rough diamond" (after CVD process)
  - .



  - 0.5 mm thick film on 7° off-axis substrate
  - surface almost free of non-epitaxial diamond
  - side length increased by about 1 mm mainly by **polycrystalline** growth
  - removing of substrate / polycrystalline rim by mechanical polishing / laser cutting

Growth on off-axis substrates IV: flexible growth conditions

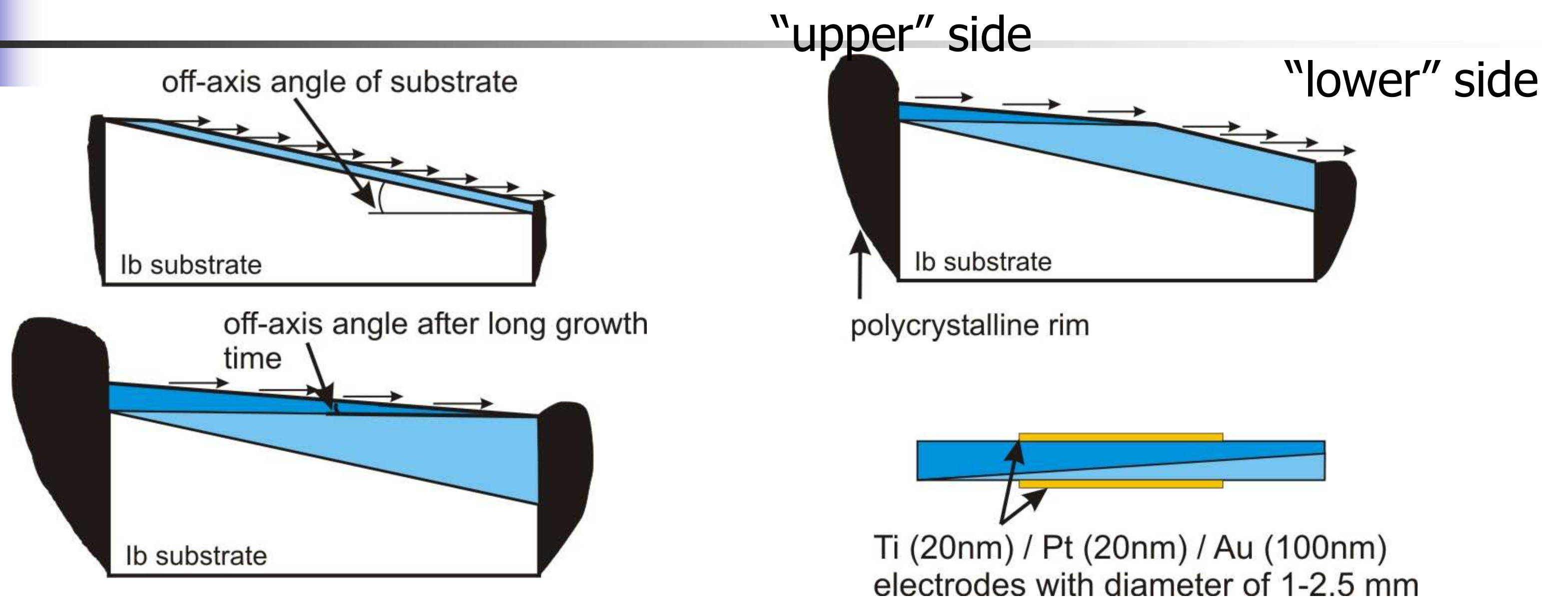


- CH_4 concentration: 5-20 %
- CO_2 concentration: 0-2 %
- samples about 400 µm thick
- **no** non-epitaxial diamond
- narrow rocking curve line widths

⇒ off-axis substrates allow a very broad range of process parameters

- two regions with different morphology

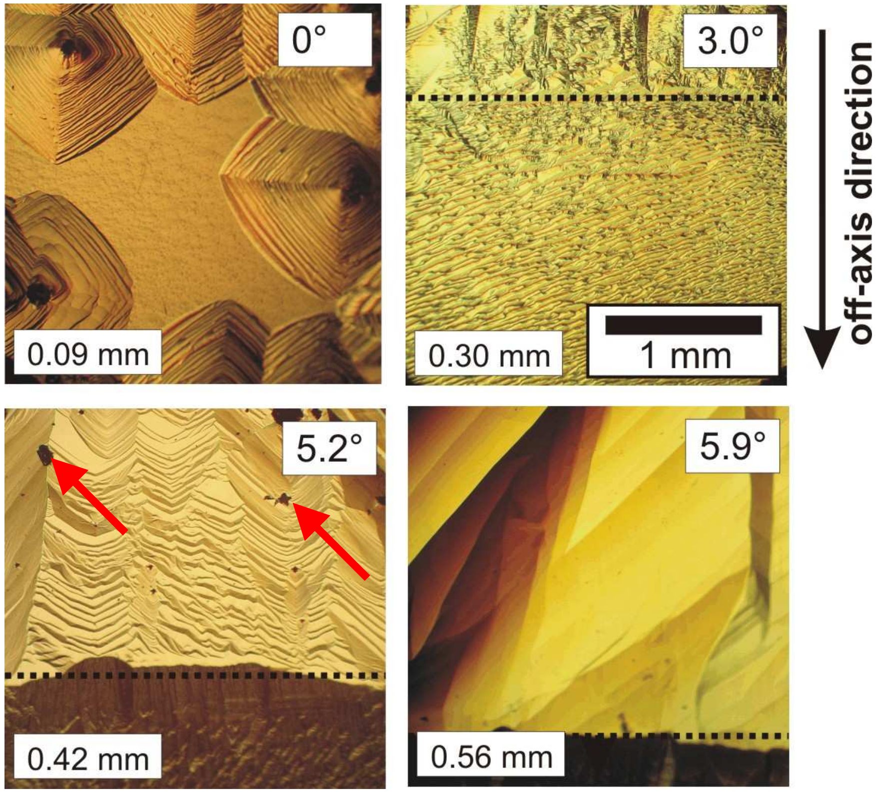
Growth on off-axis substrates V: mechanisms



- lattice planes of CVD film originate from
  - **off-axis surface**
  - **polycrystalline rim**
  - **nucleation on (001) terraces**

⇒ Inhomogeneity in structural and electronic properties??

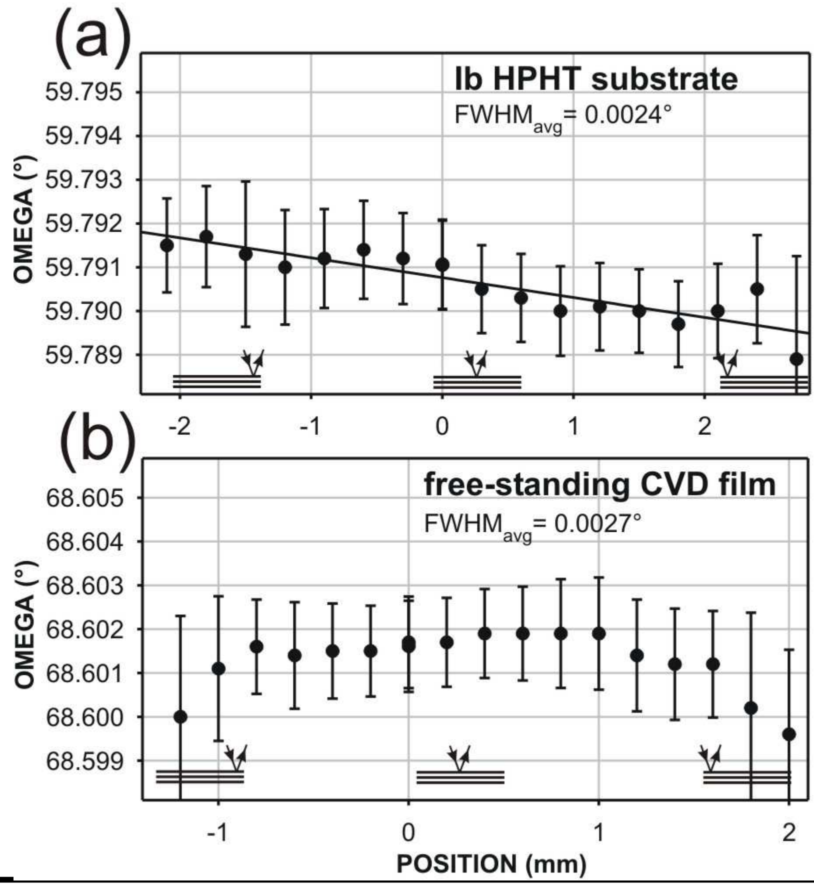
Growth on off-axis substrates VI: varying off-axis angle



- 20h growth @ 10% CH_4
- thicknesses of 0.09 to 0.56 mm
- huge improvement in growth rate
- decreasing off-axis angle during growth causes reappearance of non-epitaxial diamond
- 6° sufficient for desired film thickness of 0.5 mm

Characterisation: HRXRD

- lateral resolved measurement of diamond (004) rocking curves
- beam width: 0.2 mm
- 0.37 mm freestanding CVD film
- line widths homogeneous
- no bending of this CVD film
- line width only slightly higher than substrate (0.0027°)



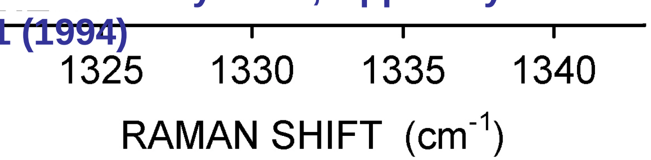
Characterisation: µ-Raman

- sample: 350 µm thick freestanding CVD film
- λ=514.53 nm
- shown: single point measurement
- average values of 10 measurements:
  - position=1332.25±0.1 cm^{-1}
  - FWHM=1.63 cm^{-1}
- position equals substrate
  ⇒ no strain (due to N in substrate)
- FWHM very low compared with other diamond samples
  ⇒ good crystal quality

TABLE I. Phonon linewidths of high quality diamonds.

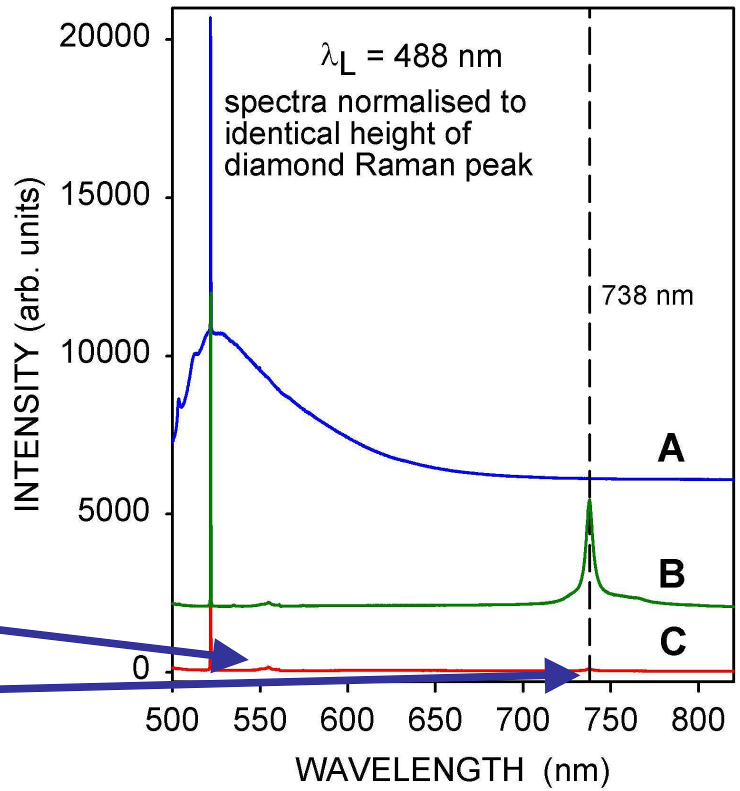
Sample[a]	Linewidth, cm^{-1} estimated error, 0.05 cm^{-1}
Synthetic Ib (Yumi)	1.68
Natural IIa (Eva)	1.87
Natural IIa (Liz)	1.92
Natural IIa (Zsa-Zsa)	2.16
Polycrystalline (Norton, Run 939)	2.31
Polycrystalline (Norton, Run 846)	2.40
Polycrystalline (Crystallume 17z05-2)	2.73
Polycrystalline (Sumitomo)	7.80
our sample	1.63

D. Kirillov & G.J. Reynolds, Appl. Phys. Lett. 65 (13), 1641 (1994)

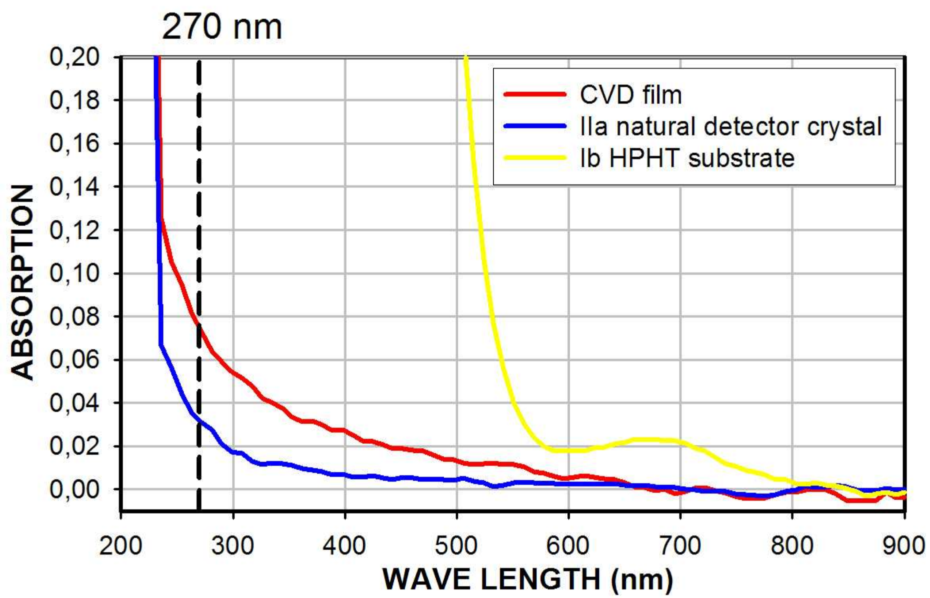


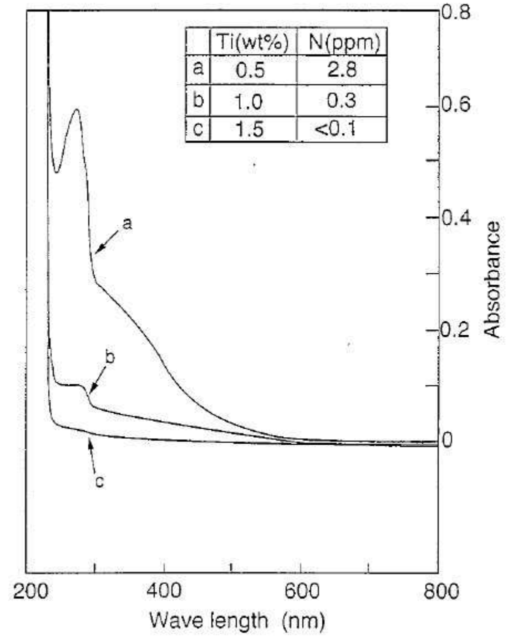
Photoluminescence

- λ=488 nm at room temperature
- normalization of spectra: identical height of Raman peak
- measured samples:
  - A: natural detector crystal
  - B: freestanding CVD-film (containing Si)
  - C: freestanding CVD-film (low Si content)
- CVD-film "C" shows only Raman peak (1st and 2nd order) and very weak Si-defect signal



Chemical purity: Nitrogen

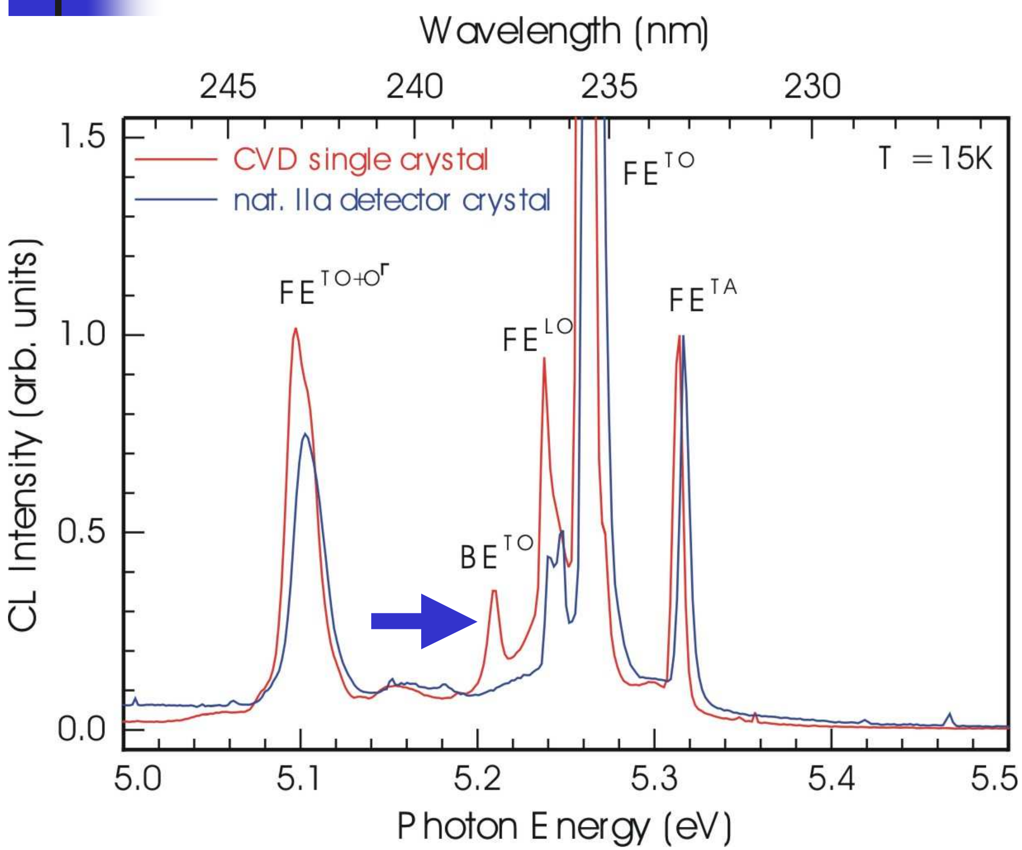




- no clear absorption peak
- N concentration of CVD film ≤ 3 ppm
- ESR measurement in preparation

H. Sumiya, S. Satoh: *High-pressure synthesis of high-purity diamond crystal*; Diamond Relat. Mater. 5 (1996) 1359.

Chemical purity: Boron

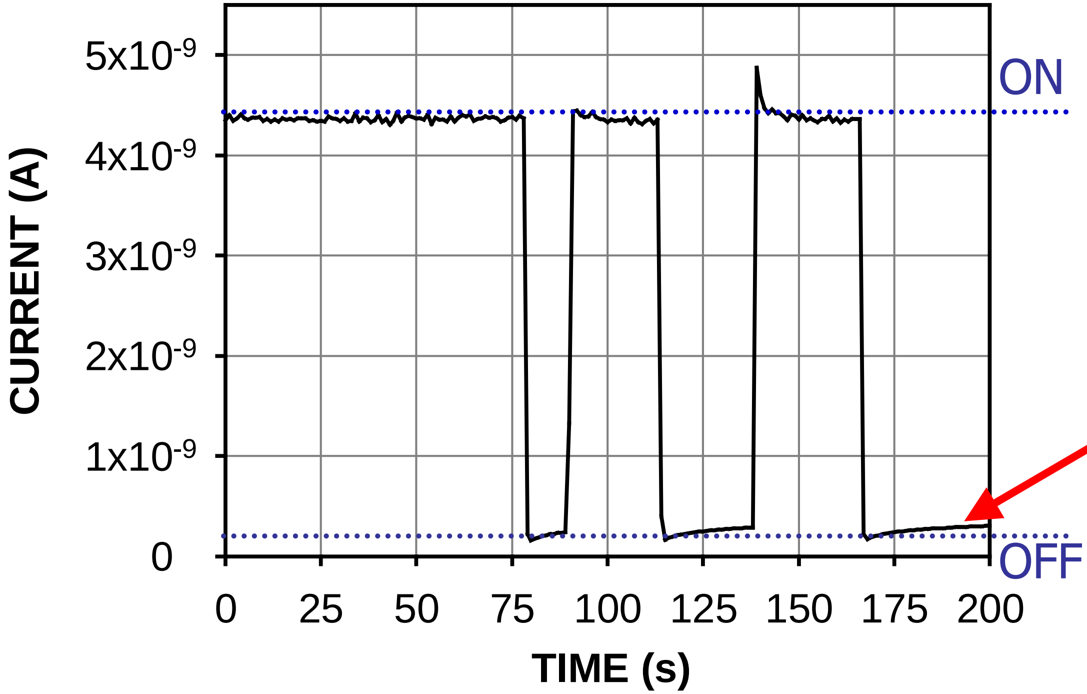


- boron concentration in ppb range
- uncompensated boron would lead to high dark currents

⇒ reducing boron contamination:

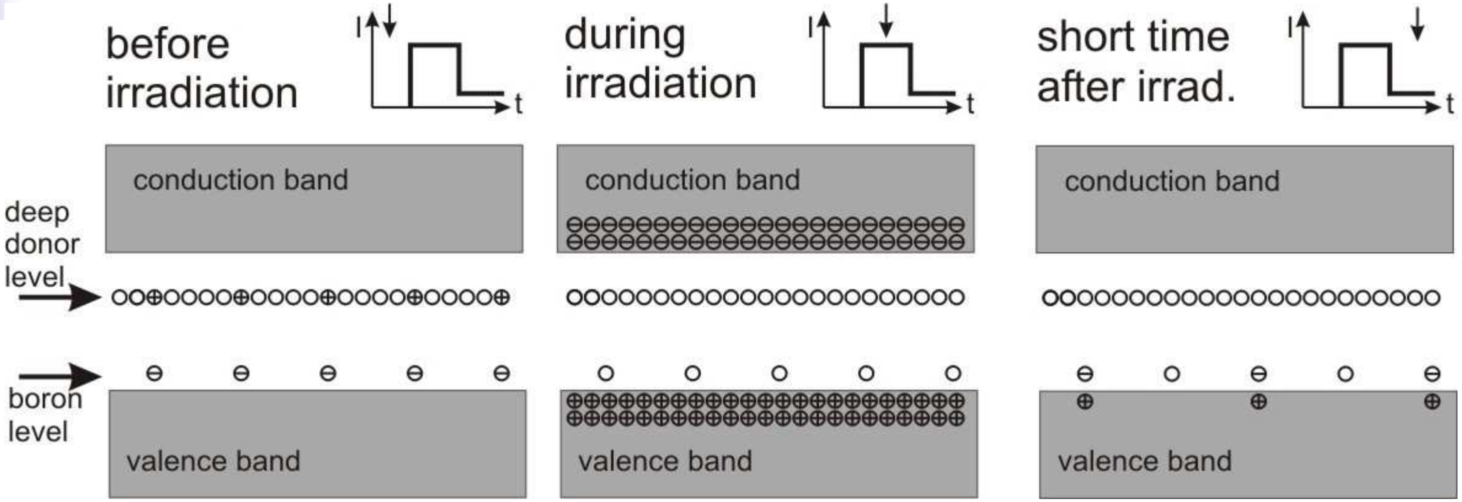
  - adding oxygen to process gas
  - removing of boron source

Detector properties I: ^{60}Co gamma



- 0.18 Gy/min, 160 V/mm
- very good sensitivity: 10^{-6} C/Gy (natural detector crystals $0.5\text{-}5\cdot10^{-7}$ C/Gy)
- fast and reproducible response
- persistent dark current of several 100 pA (before irradiation < 1 pA)!

Detector properties II: persistent current after irradiation

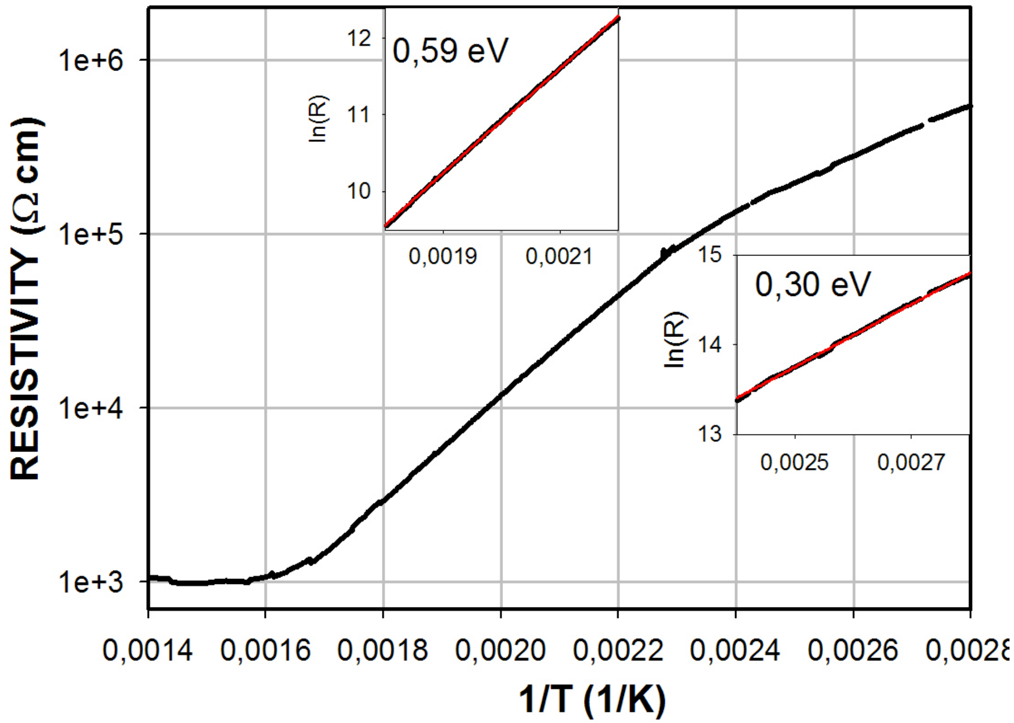


- before irradiation: boron completely compensated by deep donors (nitrogen?)
- shortly after irradiation: non-equilibrium state with many uncompensated acceptors ⇒ generation of holes in VB
  ⇒ temporarily high dark current

Detector properties III: persistent current after irradiation

- are contacts also important?
- P.J. Sellin, A. Galbiati: *Performance of a diamond x-ray sensor fabricated with metal-less graphitic contacts*, APL **87**, 093502 (2005), published online 23 August 2005
- used coplanar electrodes on polycrystalline diamond from E6
- metal contacts resulted in persistent photocurrent
- **no** persistent photocurrent for graphite electrodes fabricated by boron implantation

Detector properties IV: permanent high conductivity



- high conductivity @ RT
- boron concentration ≈ 10^{15} cm^{-3}
- activation energy in low temperature range: ≈ E_A(boron)
- boron not completely compensated
  - ⇒ very low donor density
- using as Schottky diode type detector?

Detector properties IV: single particle detection

- Results for detection of electrons and alpha particles will be presented at the talk of

  Christian Grah

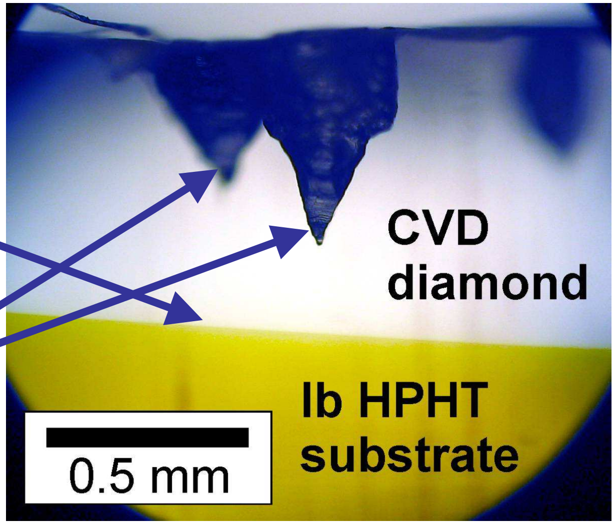
  on Thursday @ 9:30 am (Session V)

Summary

- Growth on on-axis substrates:
  - non-epitaxial diamond and pyramidal hillocks (at our process conditions)
- off-axis substrates:
  - complete suppression of NCs and PHs
  - broad range of process parameters
- Structural characterisation: CVD-films feature
  - extremely low FWHM of rocking curve and of Raman peak
  - very low photoluminescence (only very weak Si signal)
- Detector properties:
  - very good sensitivity and fast and reproducible response
  - boron causes persistent photo currents and low resistivity

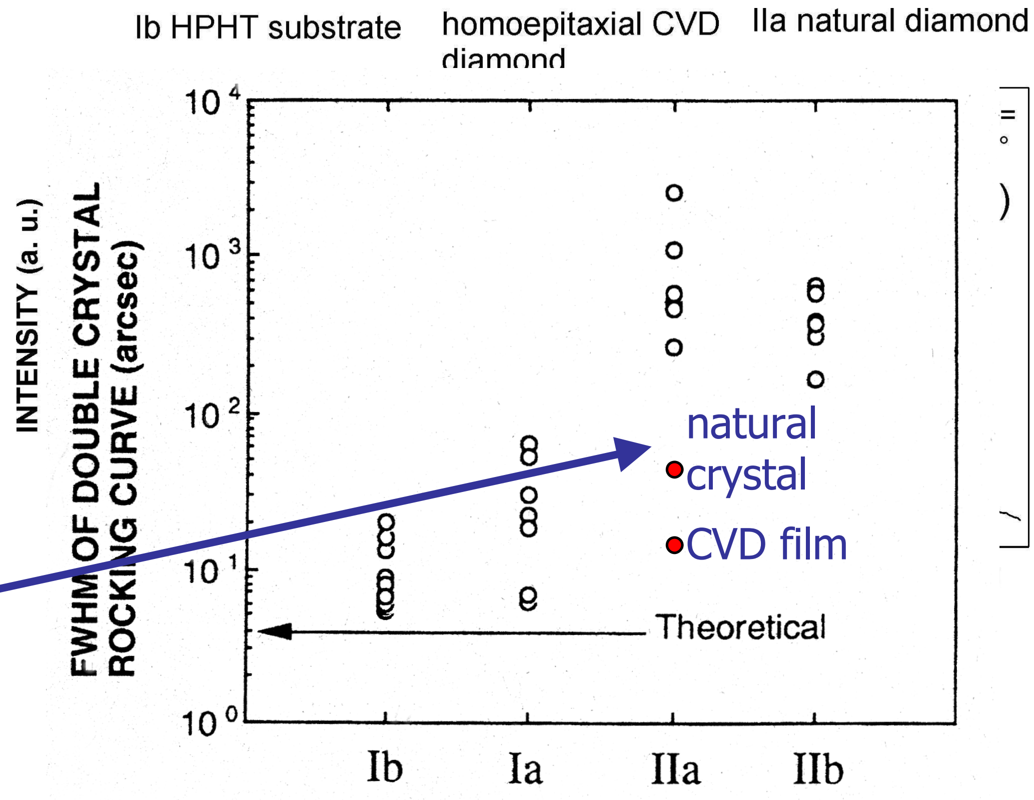
Growth on off-axis substrates III: origin of non-epitaxial diamond

- diamond after mechanical polishing
  - sharp transition between yellow (nitrogen containing) Ib substrate and transparent colorless homoepitaxial diamond film
  - dark pyramidal holes → NCs broken out during polishing process
    - NCs continuously increase in lateral size during deposition process
    - growth of NCs not necessarily starts directly on Ib surface ⇒ nucleation of NCs at **local instabilities or impurities of the growing film** (not at structural defects of substrate)



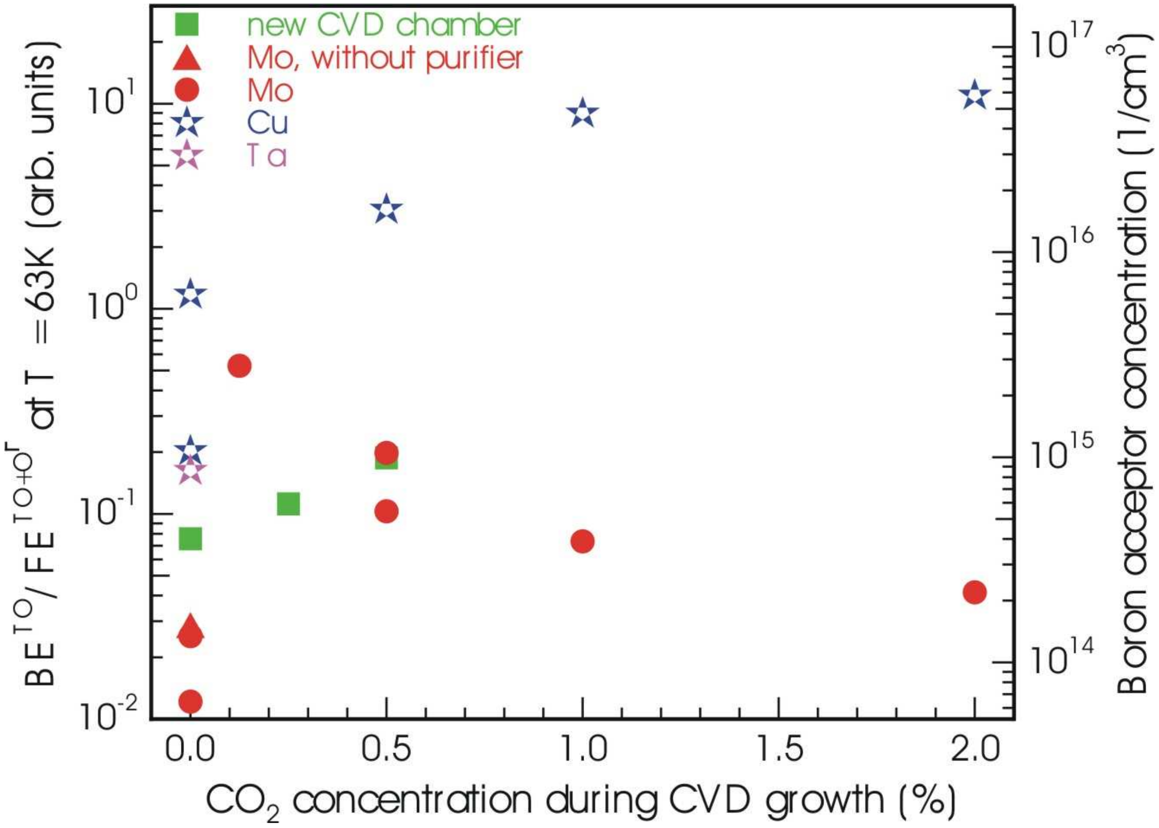
Characterisation: HRXRD I

- diamond (004) rocking curves
  - CVD film: 560 µm thick, removed from substrate
  - IIa natural diamond: used as detector crystal
  - FWHM of natural diamond and CVD film **extremely low** compared with other IIa crystals



S. Fujii et al., Appl. Phys. A 61 (1995) 331

Chemical purity: Boron



- measures to decrease B contamination:
  - increasing gas purity
  - adding CO_2 to process gas: Possible etching of the boron source? Removing of B source with CO_2 plasma?
  - replacing parts of the sample holder
  - new CVD chamber
- next steps:
  - thorough cleaning of old CVD setup