SC-CVD growth and diamond devices

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Outline

1. SC-CVD diamond growth: diamond for electronics

2. Growth of n-type diamond

3. p-I-n; junctions and their characteristics

2. UV detector applications for space

1. Synthetic diamond

- Stone
  - Simulant
  - Diamond
    - Synthetic
      - HPHT
      - CVD
    - Natural
      - Treated colour
      - Natural (non-treated) colour

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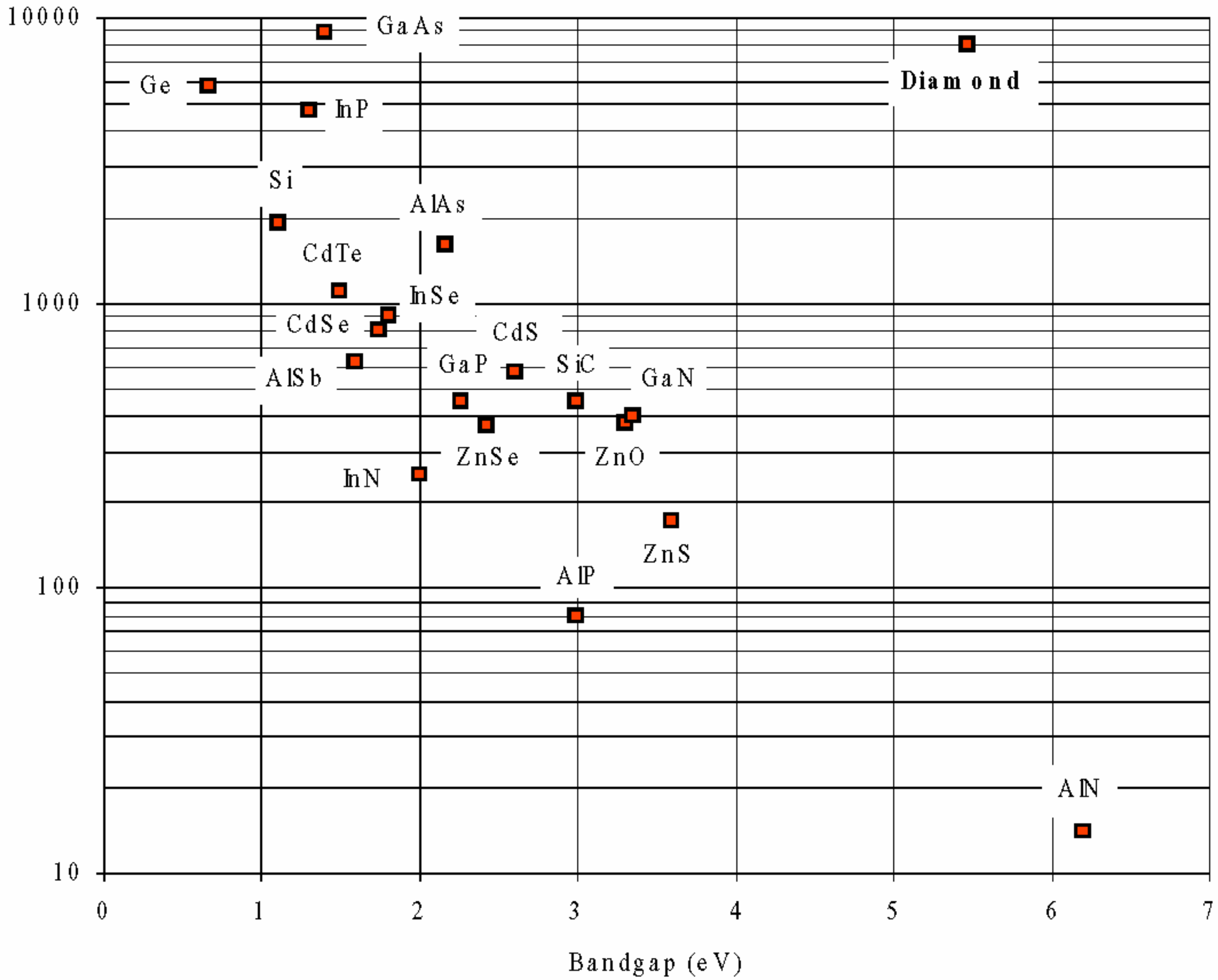
Diamond the only wide bandgap high mobility materia

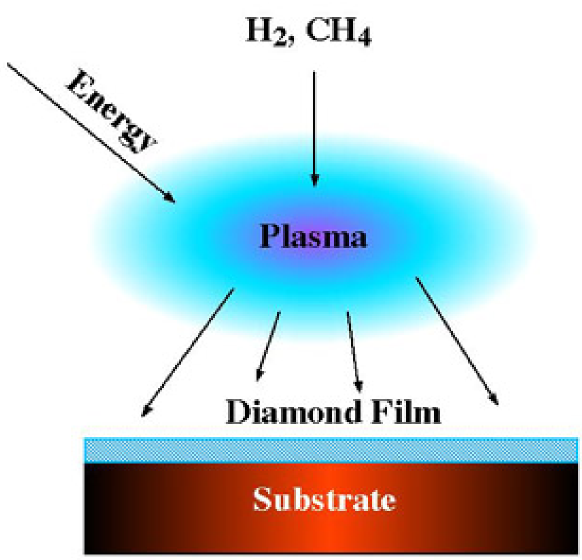


Synthetic diamond

HPHT synthesis | CVD synthesis

2. Chemical Vapour Deposition (CVD)

Pressure : 50-200 torr
Temperature substrate : 800-1000°C
Gas: CH_4(0.05-10% CH_4) +H_2 ......+O_2, Ar,..



Gas -> diamond

The deposition of diamond from a carbon containing gas mixture.

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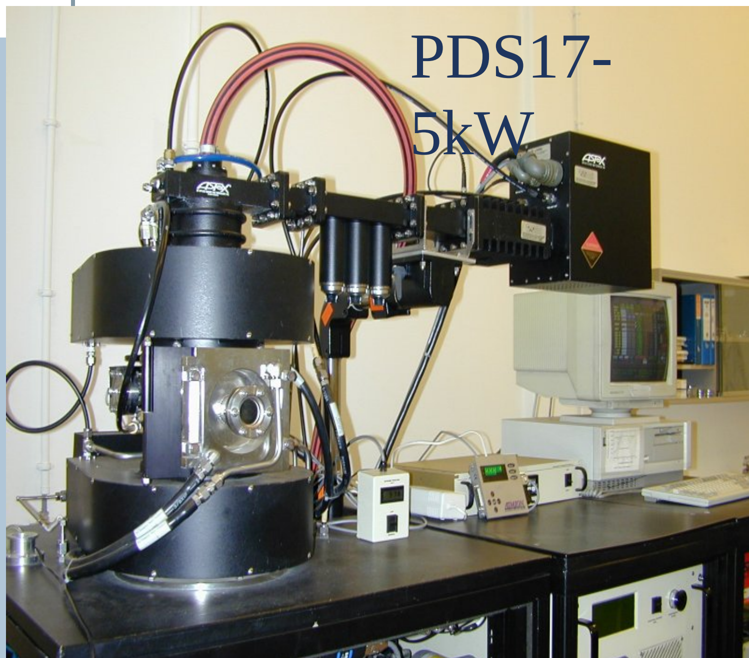
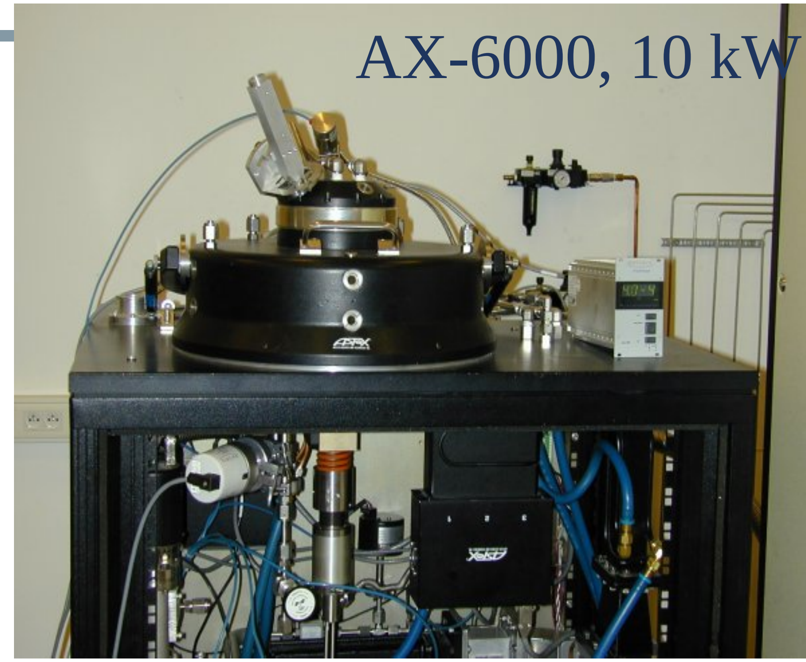
MW-PACVD SET up





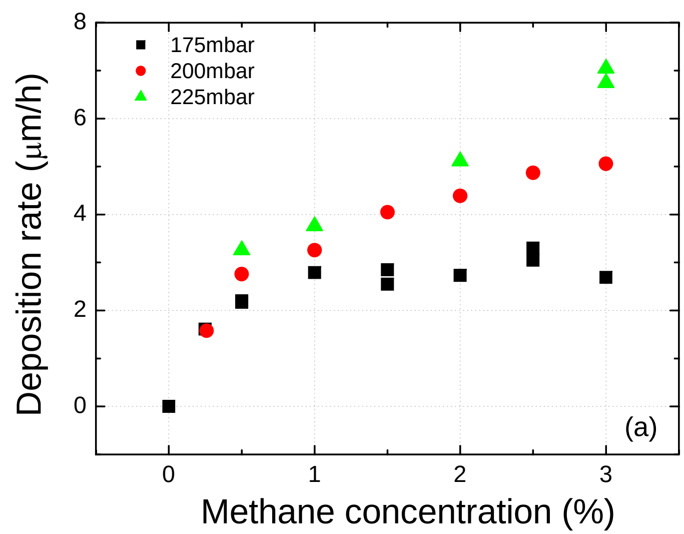
Key issue

preparation of high quality CVD diamond films

equivalent to type IIa natural diamond

with - low intrinsic defect concentrations

- active incorporation of dopants



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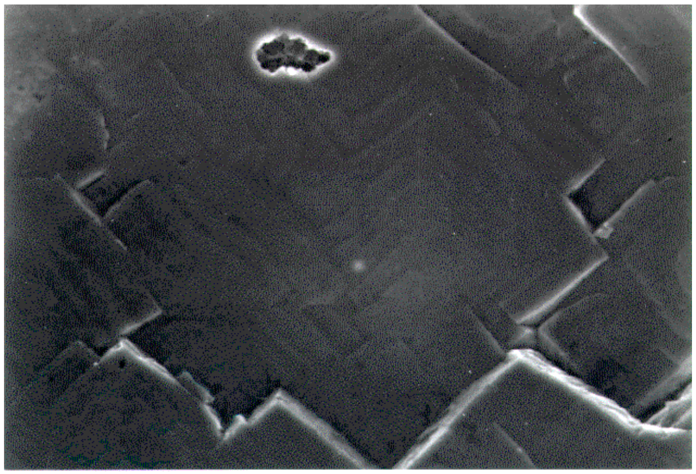
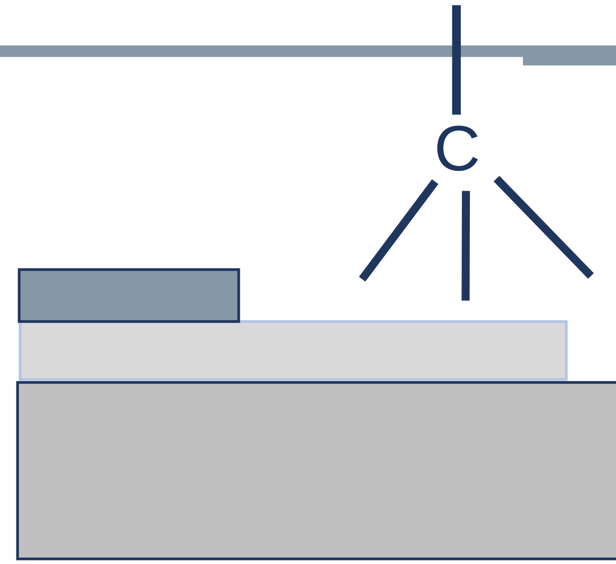
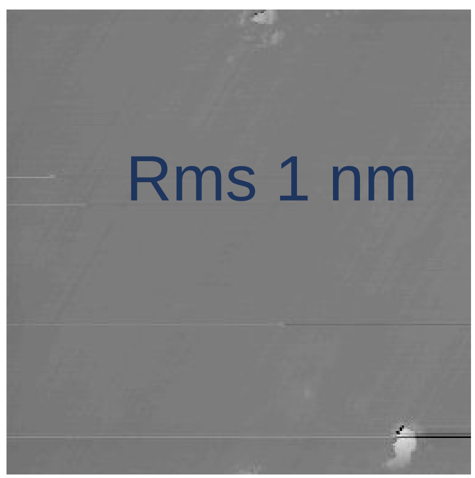
Single crystal CVD diamond growth on 100 surfaces





Growth by a step flow: coalesence of macrosopic steps



Surface pretreatment,

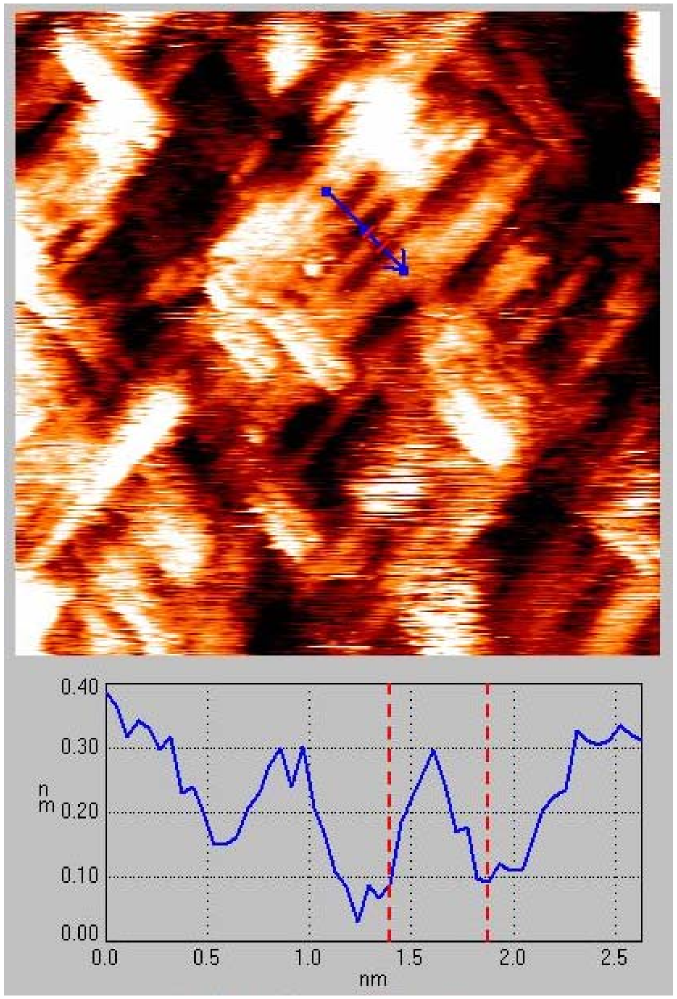
Substrate quality, missorientation angle

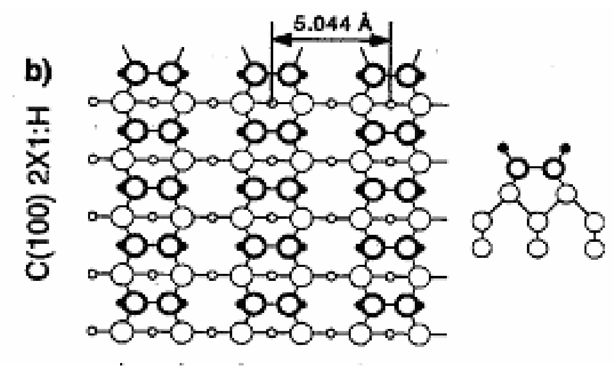
Step- growth & hydrogenation

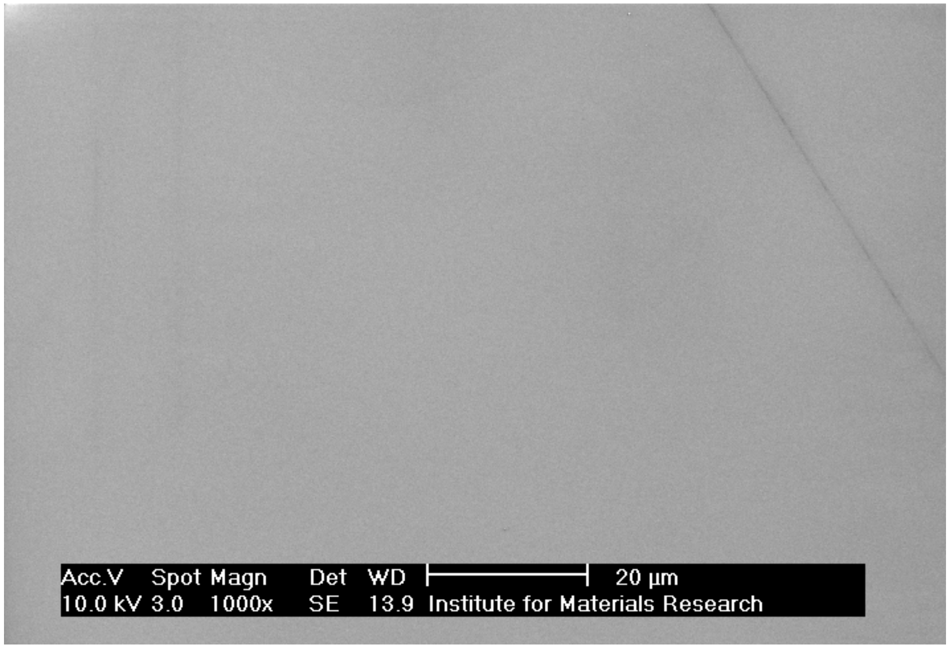
- terraces separated by monoatomic steps.
- **2 x 1 reconstruction:**

the domains are rotated relative to each other by 90º.

- **clearly are the “cigars” on the flat area’s. These are the bright lines.**
- **Distance between the “cigars” is 5.0Å.**
- **Height = 2Å.**







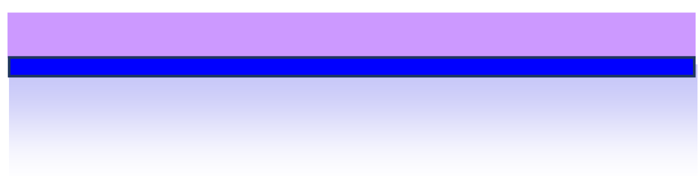
High quality CVD diamond single crystal layer
50 μm thick 4% CH_4 in H_2, 150 torr

Free standing CVD diamond single crystal growth

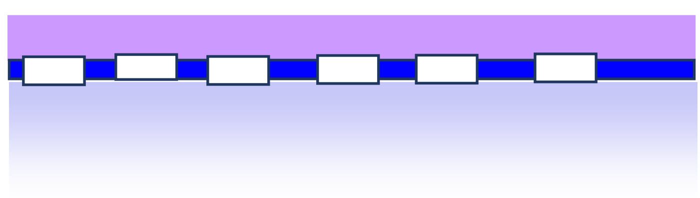
Growth: optimisation of plasma; growth rate -> Thick films

Lift-off of the epilayer from the substrate:

1) laser cutting
2) Ion implantation
3) Etching



MeV ion implantation
-mechanicaly week layer



Messa litography and
RIE etching in O_2-plasma

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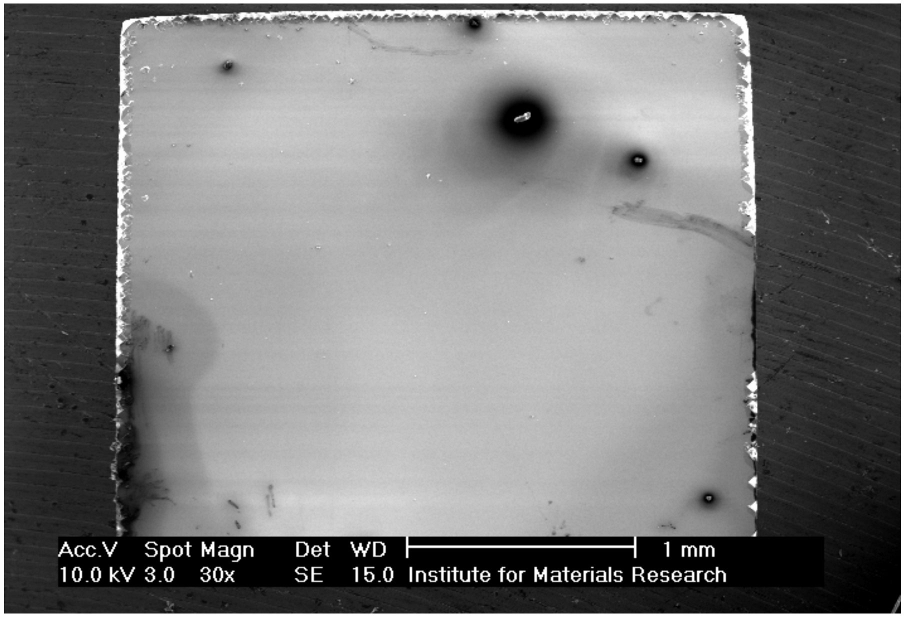
SC-CVD growth



p: 160 torr
5%CH4 in H_2
T: 850°C
250 μm

- Low growth rate 0.2-0.3 μm/hour: high quality surfaces
- High growth rate: 10-20 μm/hour: optimisation of hillock (H) and unepitaxial crystal (UC) density (Surface treatments,growth conditions)

DOPING OF SINGLE CRYSTAL DIAMOND

***Phosphorous* doped {111} homoepitaxial diamond**
Boron doped {111} and {100} oriented diamond

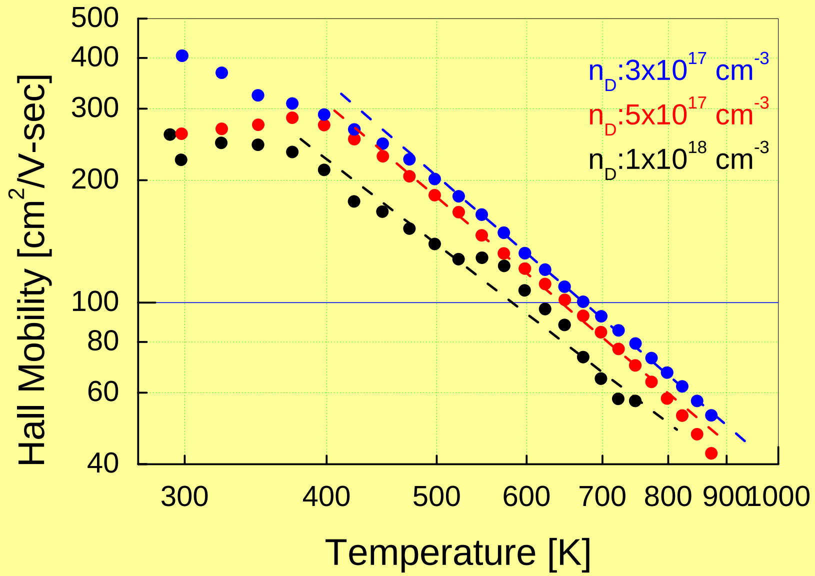
***pn*-junction**

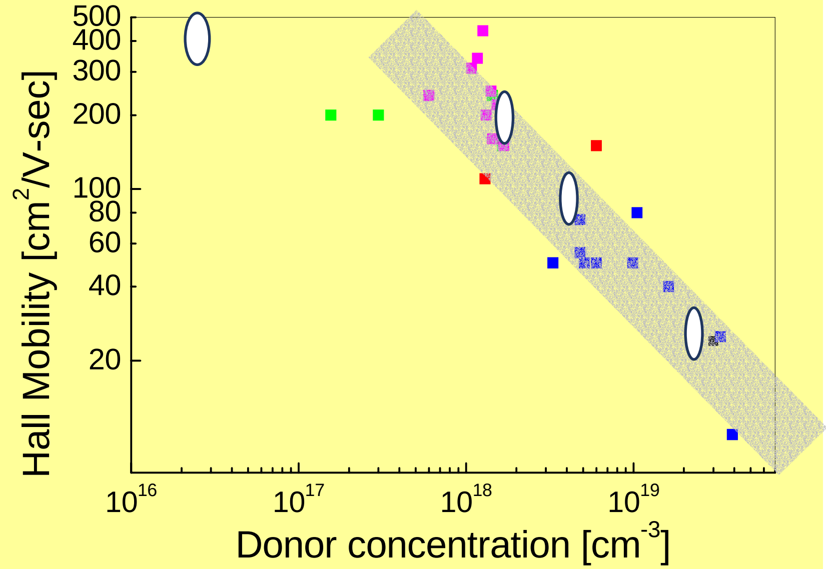
Active electronic devices,
high power, high frequencies,
high temperature operation

Ultraviolet LED
235 nm (Koizumi et al Science 2001)

Solar blind UV sensor

Optimization of of *n*-type diamond - carrier mobility





$\mu \sim T^{-(2 \sim 2.4)}$

$\mu \sim n_D^{-1}$

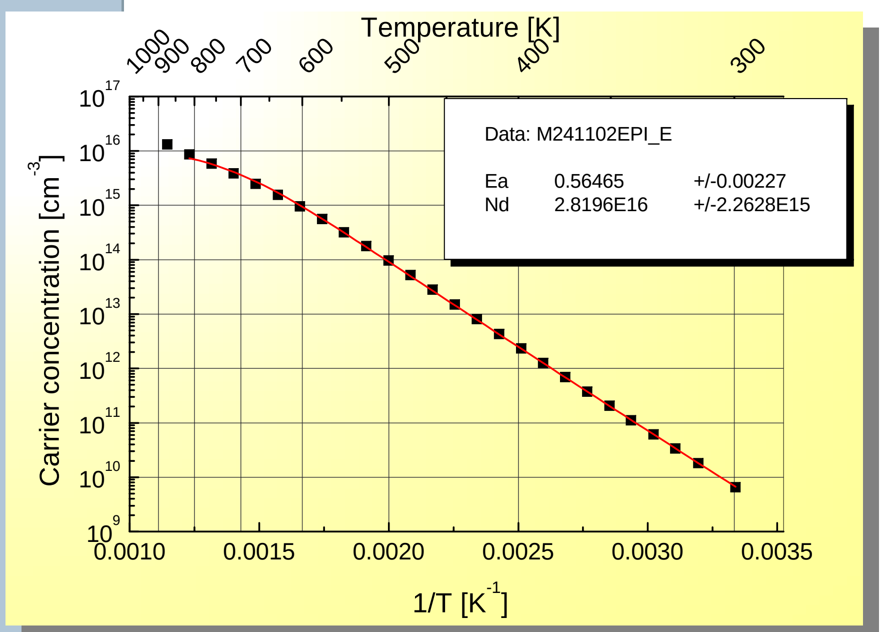
Comparison of IMO (Be) and NIMS(Japan) results

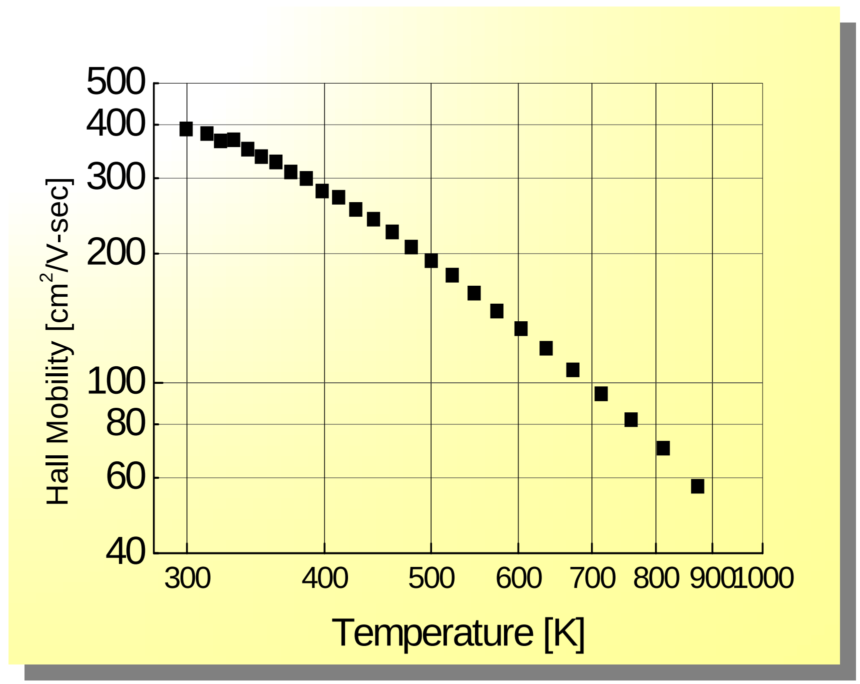
Carrier mobility of (111) n-type diamond

- Growth at IMO, ASTeX, 5kW reactor
  - P: 600 – 800 W
  - p: 100-120 Torr
  - T: 860 – 880 °C
  - CH_4/H_2: 0.05 – 0.15 %
  - PH_3/CH_4 : 2 – 2000 ppm
  - TMB/CH4: 2-2000ppm

N_P: $3x10^{16}$ – $5x10^{19}$ cm^{-3}

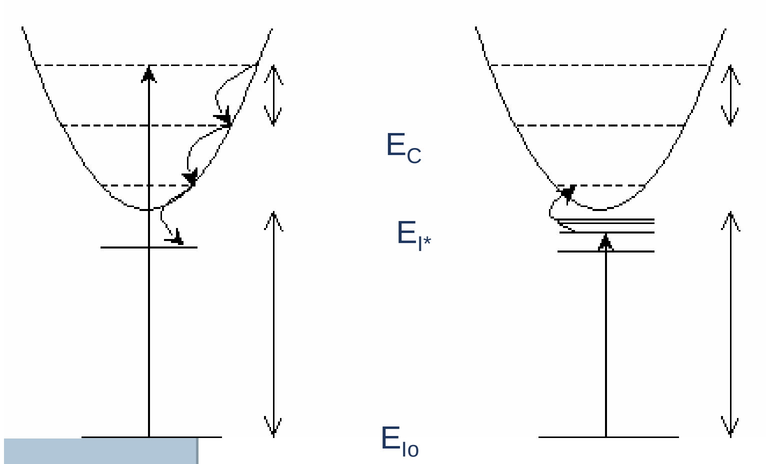
µ: ≈ 400 $cm^2V^{-1}s^{-1}$

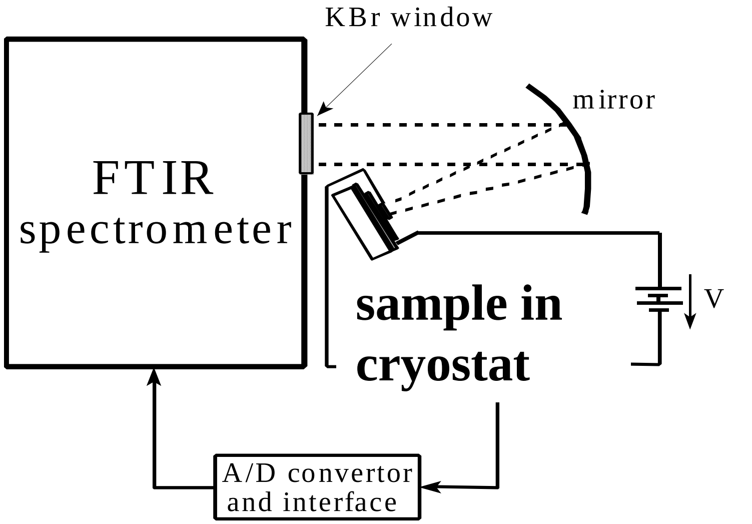


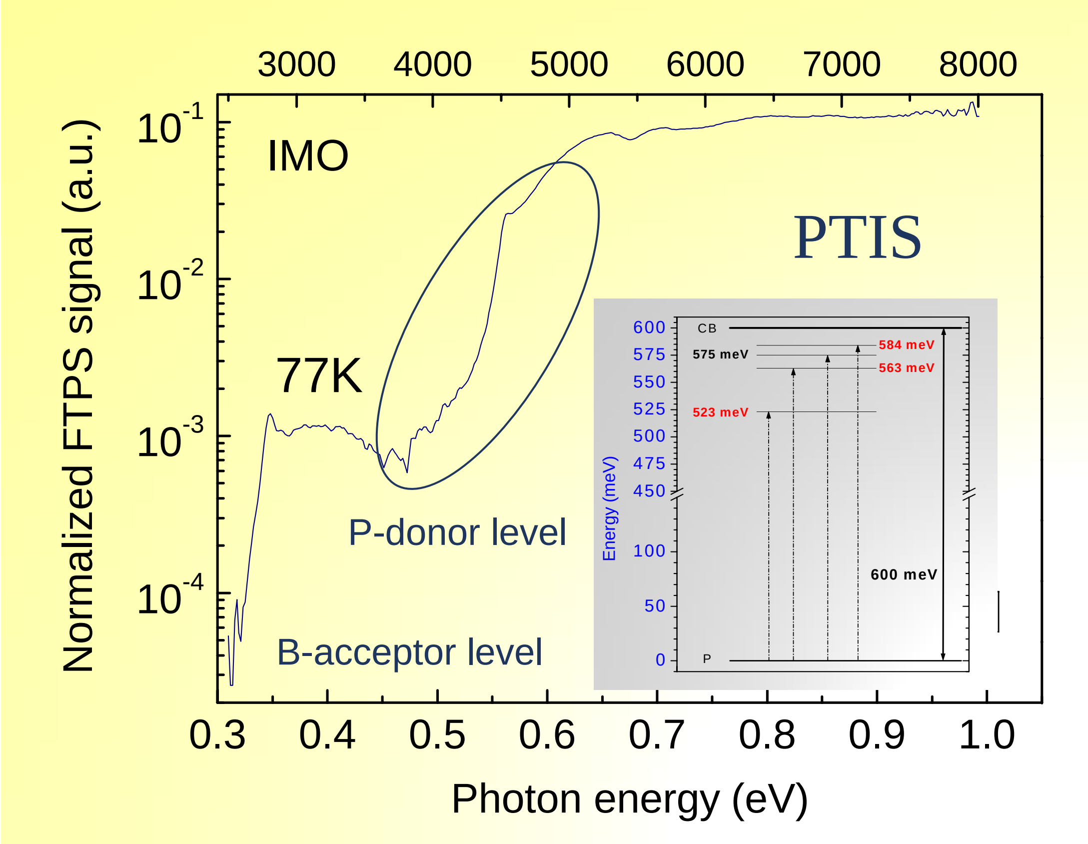


Fourier Transform Photocurrent Spectroscopy

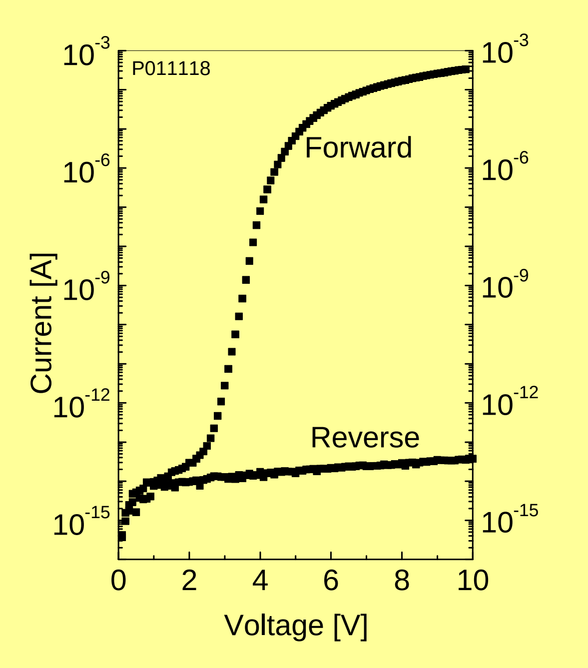
PH_3-H_2-CH_4
P6-doped CVD diamond layer, 15µm
S.Koizumi: 400ppm gas phase, 0.5 W
IMO P6: 800ppm gas phase, 3 kW





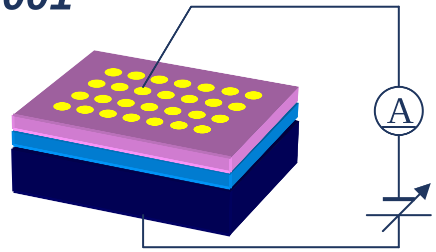


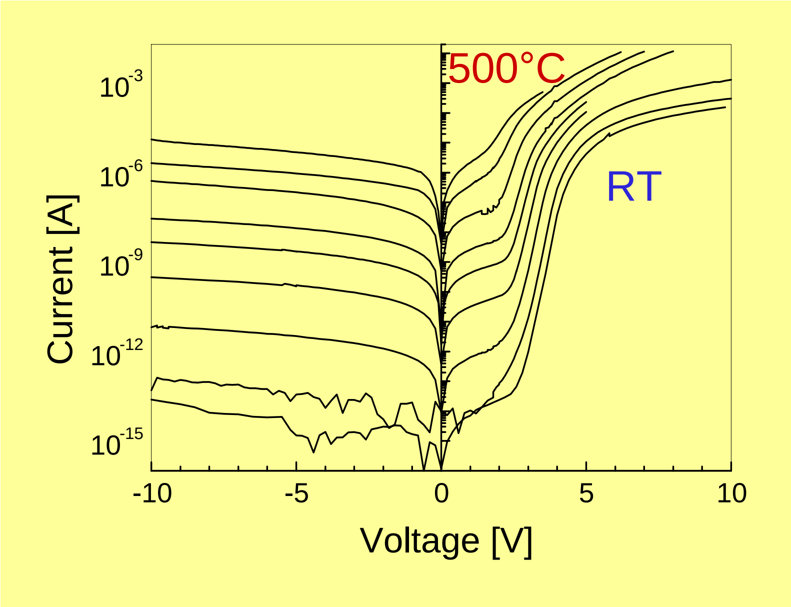
I-V characteristics of diamond *pn*-junction diode



Koizumi at al, Science 2001

- turn-on voltage: 4.5~5 V
- breakdown voltage: > 100 V
- rectification ratio: > 10^{10} at +/- 10V
- Ideality factor (n): ~3.5 -> 1.5 (500°C)
- large series resistance: ~10^5 Ω





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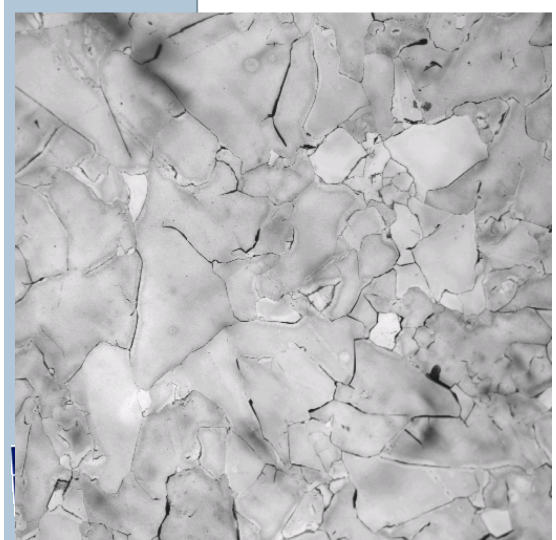
Growth of polycrystalline n-type diamond

- Proces parameters
  - P: 800W, p: 100 Torr
  - T: 850 – 900 °C
  - PH_3/CH_4 : 100 – 500 ppm

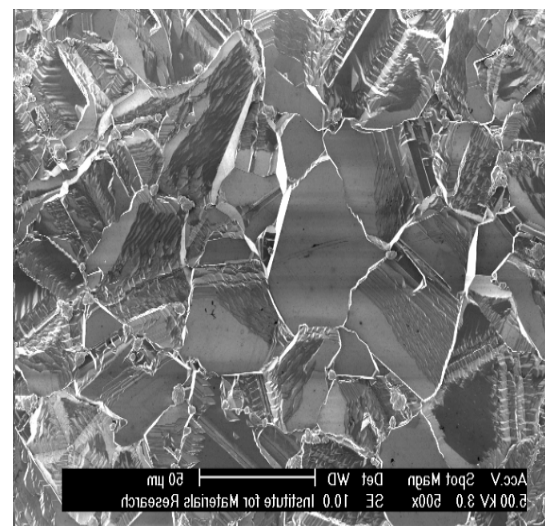
Si: CVD diamond 2 inch



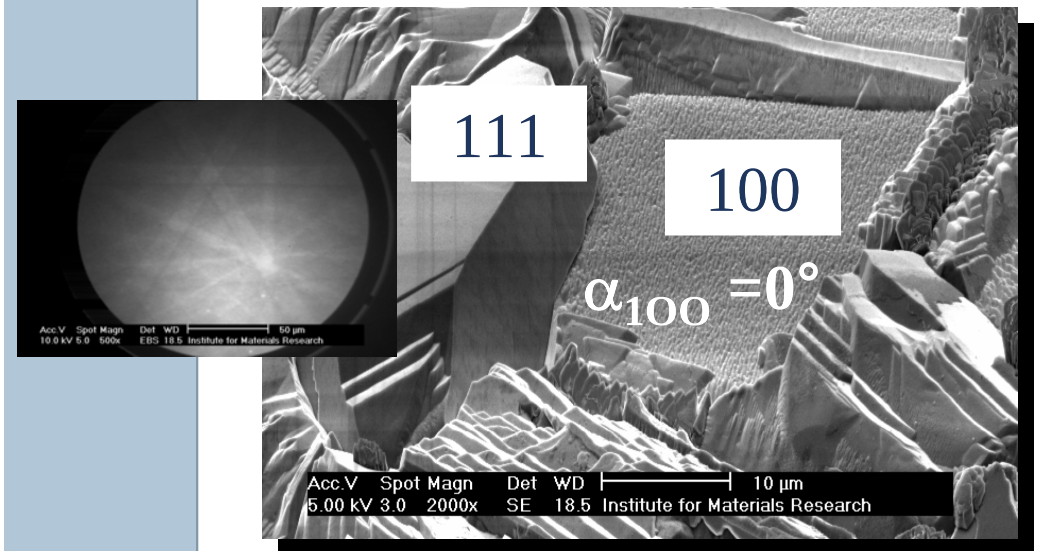
Free standing polished substrate
preferential (110)
(intrinsic or B-doped)

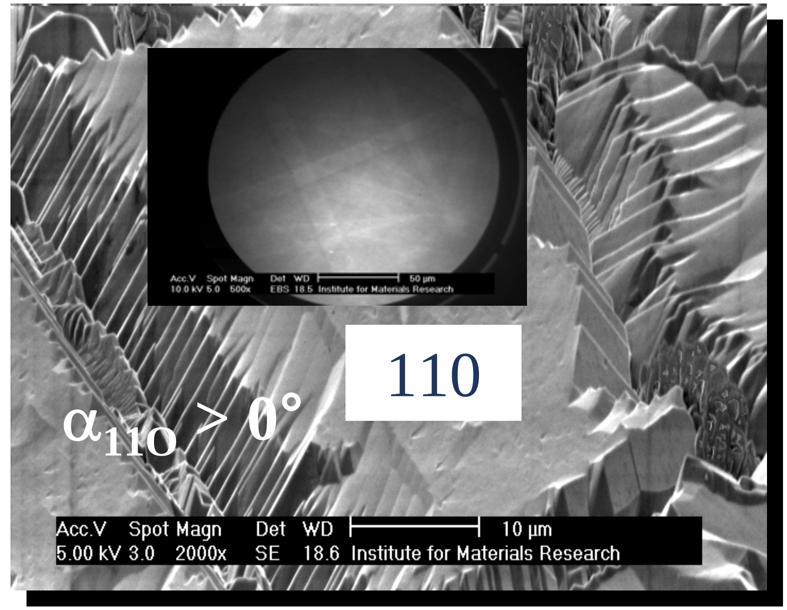
3 µm P-doped CVD diamond film

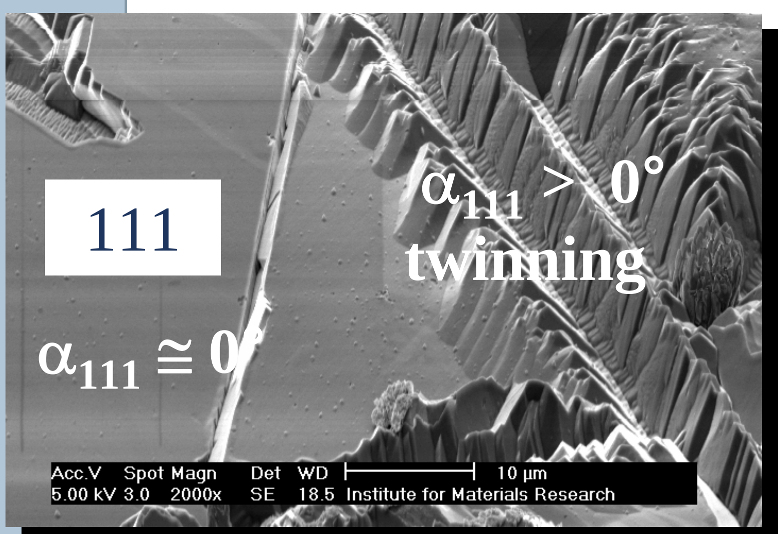
Growth mechanism?



SEM & ESBD





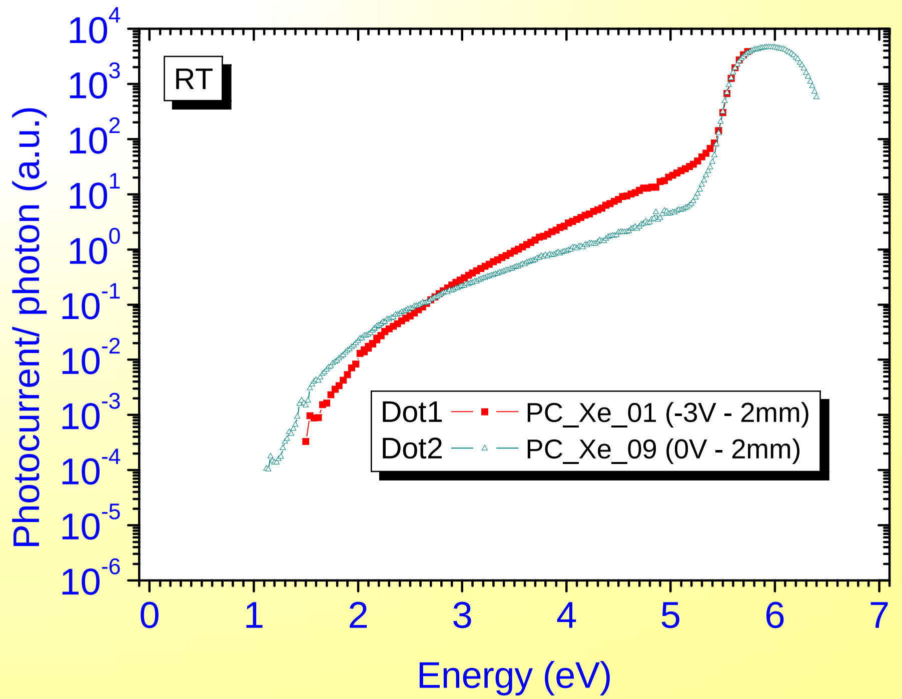


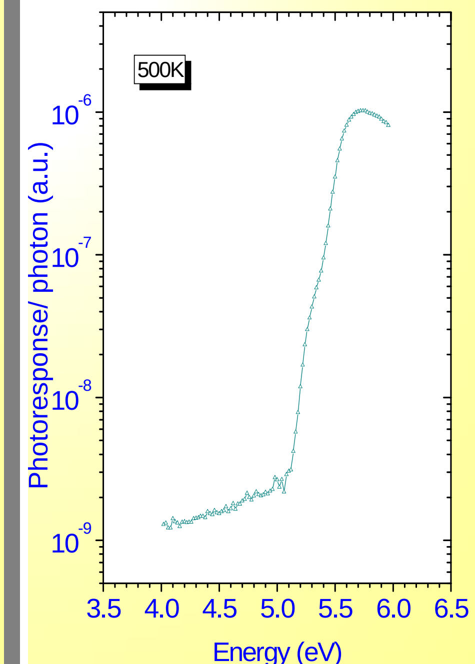
Polished substrate: preferential (110)

α = angle between the growth surface and and the crystal plane

Substrate and grain orientation!

UV properties -polycrystalline pn-diode





Polycrystalline pn-diode, R=1mm

Dot 1: 5 orders rectification

Dot 2: 7 orders rectification

Response time < 1 e-6 sec

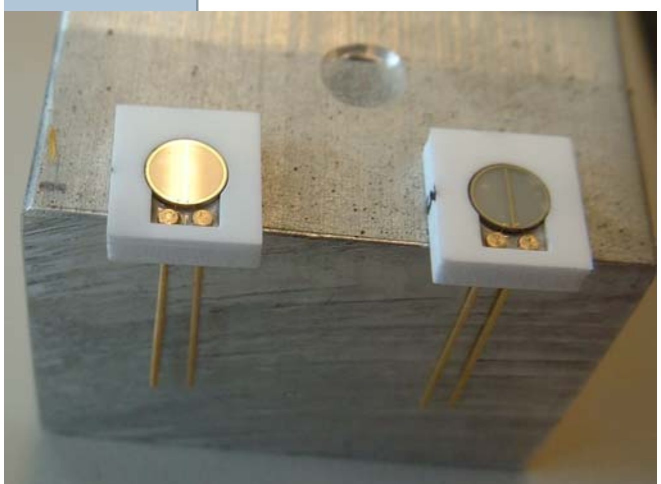
1.2eV:
onset of Dx defect in polycrystalline CVD diamond

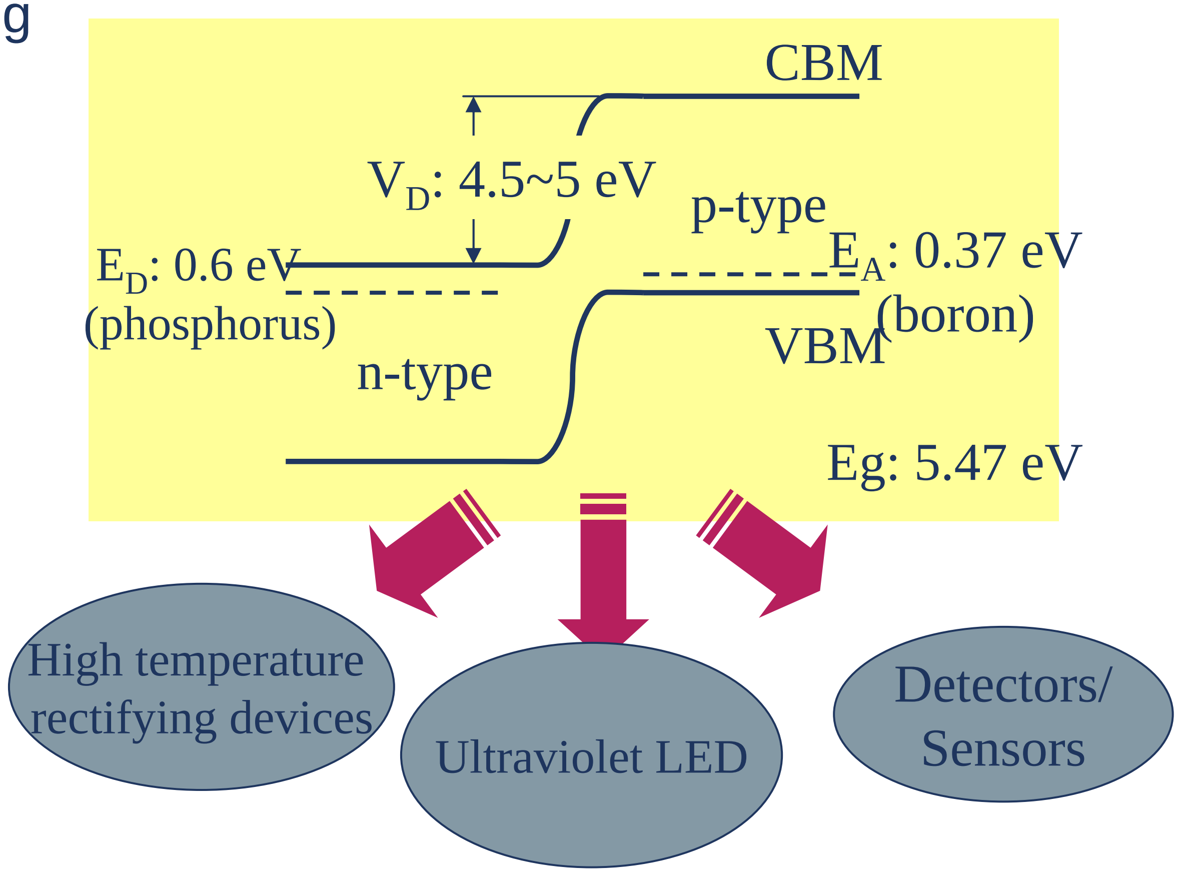
M. Nesladek
Appl. Phys. Letters 72, 25 (1998) 3306-3308

CVD pn junction type detector for UV sensor for space applications (LYRA-PROBA II)

Comparison with "undoped" detector devices:

1) High collection efficiency of generated charge
2) Temperature stability, linearity
3) Fast response (no persistent photocurrents ?)
4) No priming ?
5) 3D processing





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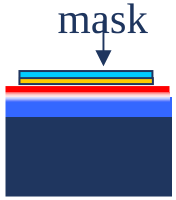
Optimisation of the homogeneity,processing and contacts on 5mm HPHT substrates

HPHT diamond substrate

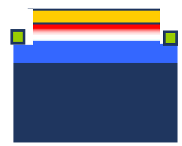
Growth of p-type CVD diamond epilayer

Growth of i and n-type diamond epilayer



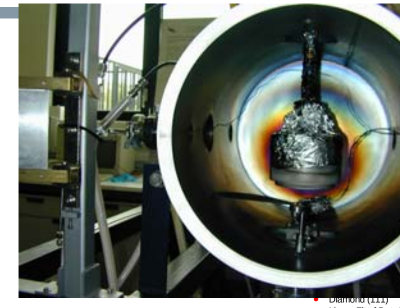
Vacuum deposition (EB)

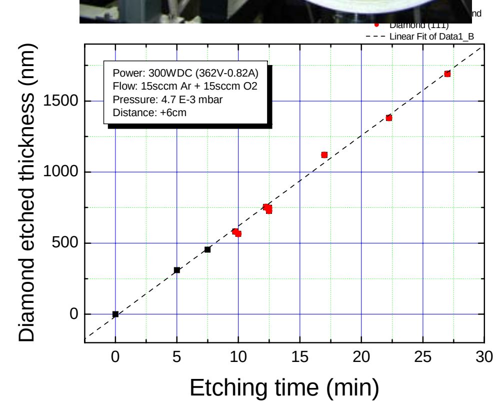
Reactive ion etching Of n-type layer



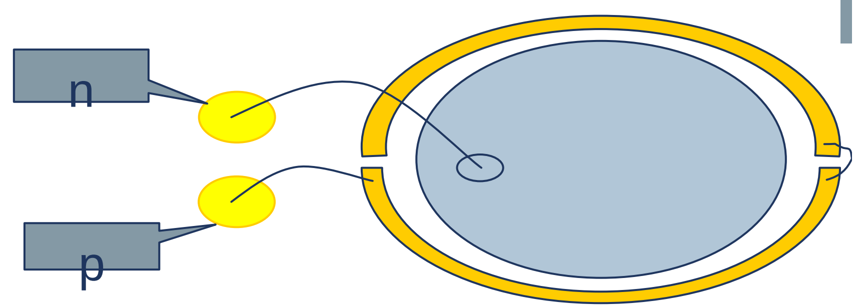
Chemical etching and 2nd contact deposition

Ti/Al/Au
C/Al/Au
Si/Al/Au





mesa
(200 μm – 5mm)



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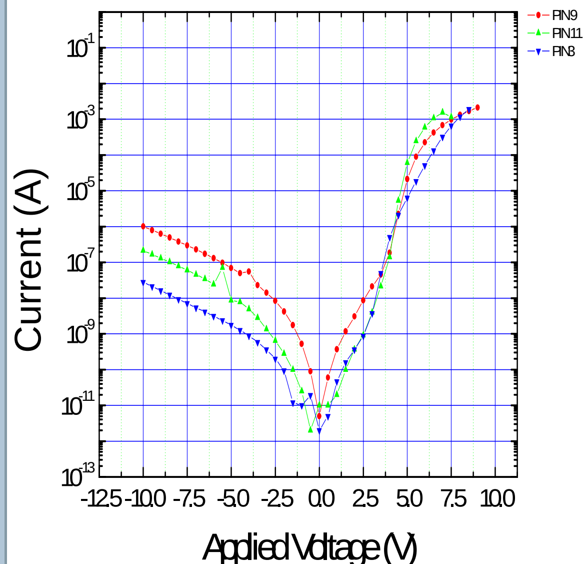
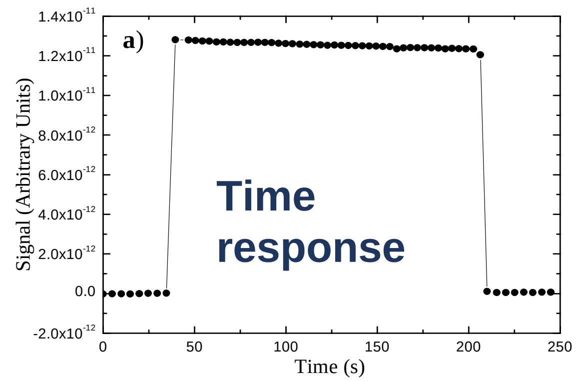
IV and photoresponse characteristics of diamond pn junction sensors

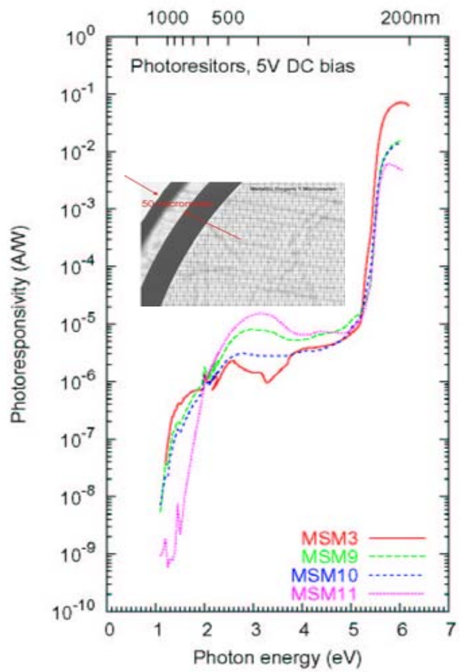
I- V characteristics



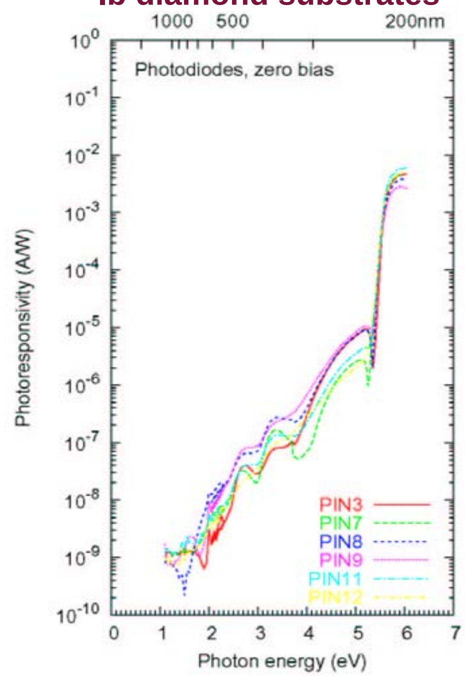


Responsivity In VIS- UV

Epilayer on IIa diamond substrates



Pin epilayer structure on Ib diamond substrates



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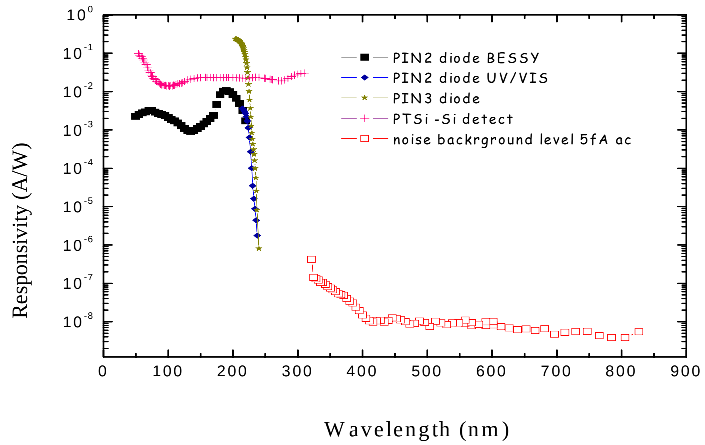
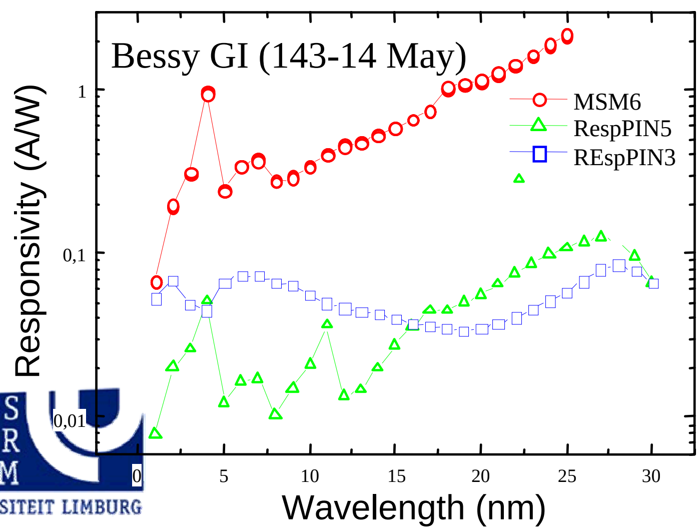
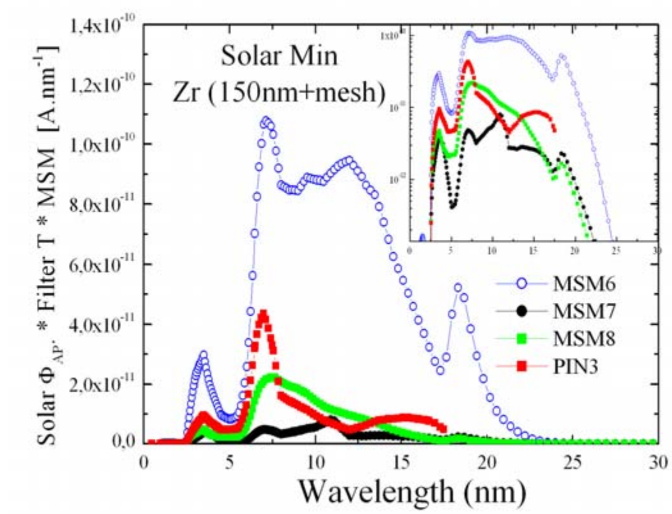
Responsivity of detectors in XUV

Tests XUV-UV
BESSY/ NIST





Response to solar XUV spectra
(3 mm aperture)



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Summary

- SC-CVD diamond growth
  - Optimisation of SC CVD diamond growth for detectors applications
  - (100) surfaces: free standing CVD diamond plates
  - (111) surfaces: n-type doping and junction fabrications

- PN junction optimsation
  - Reproducible P-doping on {111} surfaces, a smooth surface, mobilities 400 – 500 $cm^2 V^{-1} s^{-1}$ for $N_d = 10^{16-17} cm^{-3}$)
  - pn-junctions with good rectification ;
  - n-type polycrystalline diamond and pn junctions: pn-junctions with good rectificatio and diode ideality factor of n_{RT}=2.9. Dx defect (influencing I-V characteristics),

- UV detectors:
  - UV- XUV Responsivities close to Si diode
  - Excellent solar blidness
  - Fast and stable response

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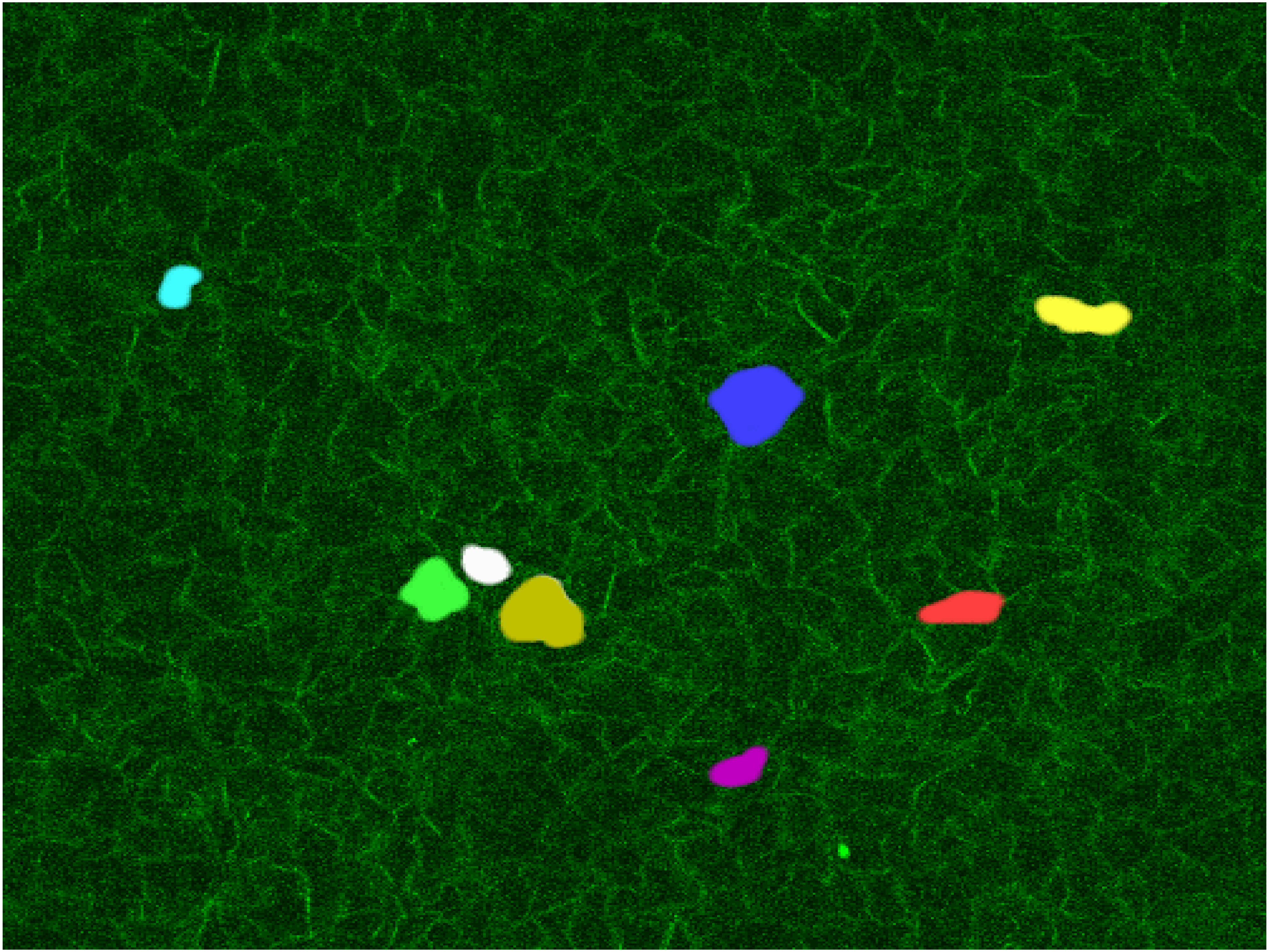
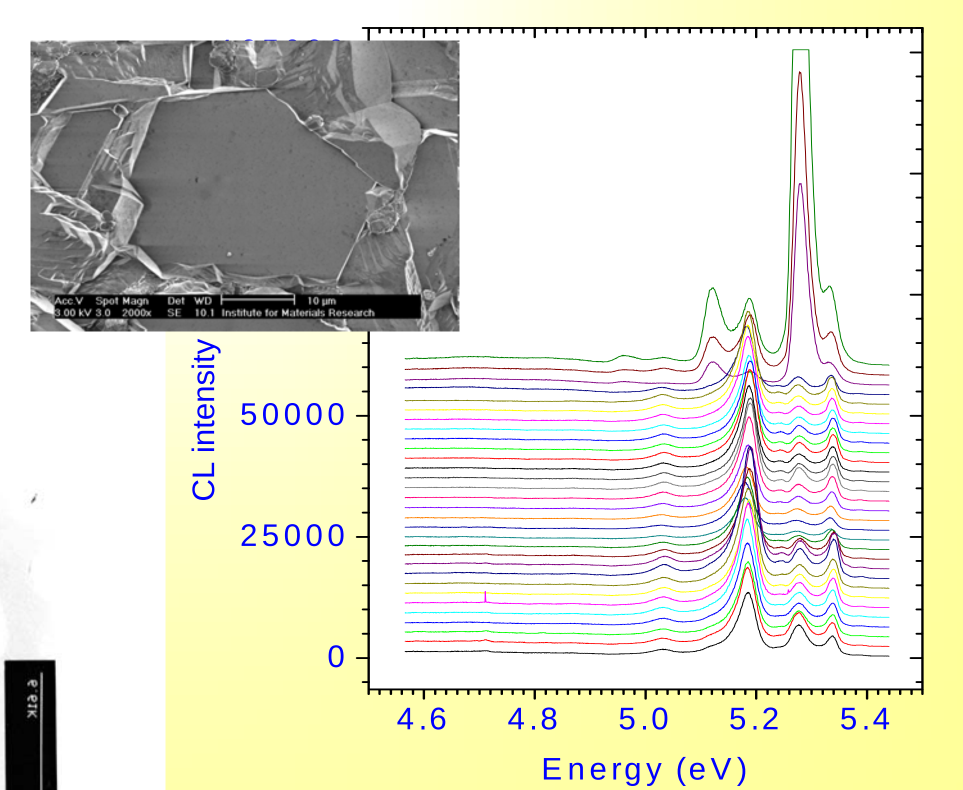
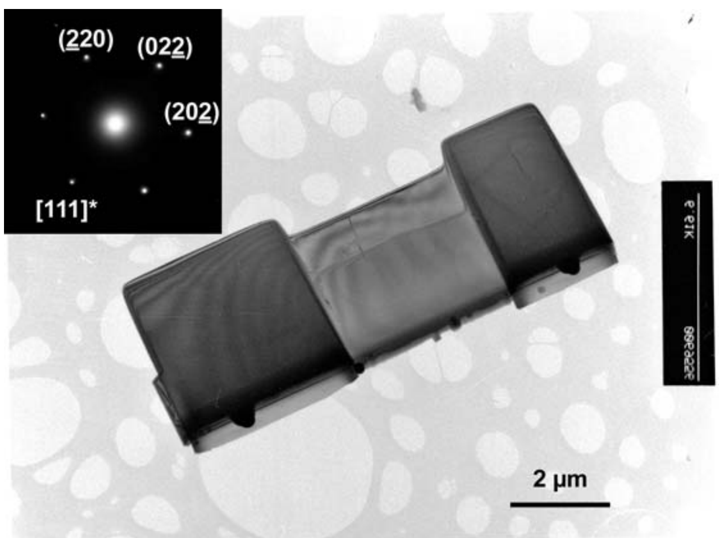


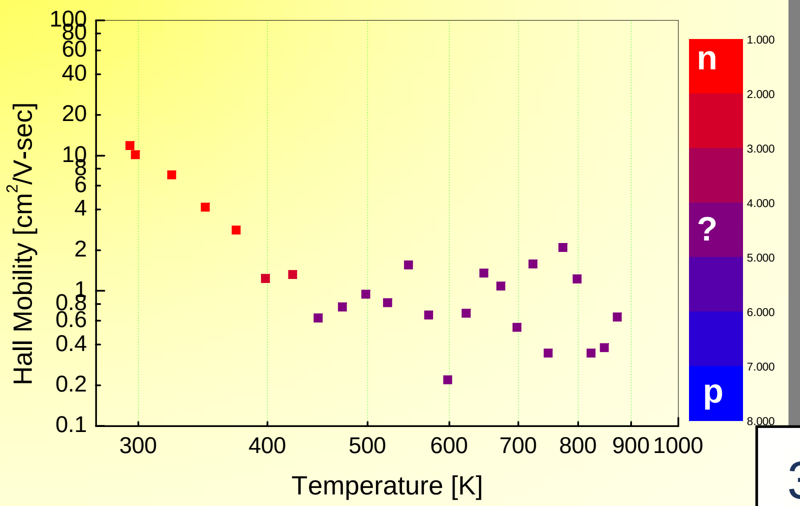
TEM view of diamond (110) grain

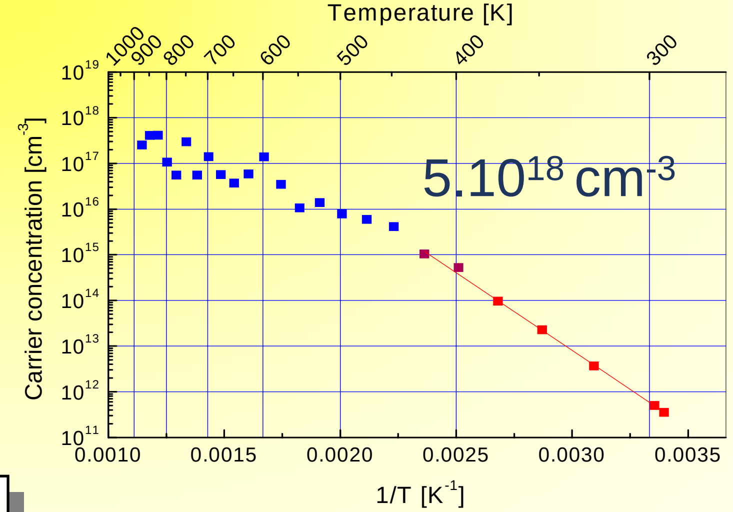




FIB prepared TEM polycrystalline junction

Hall measurements on P-doped IMO films

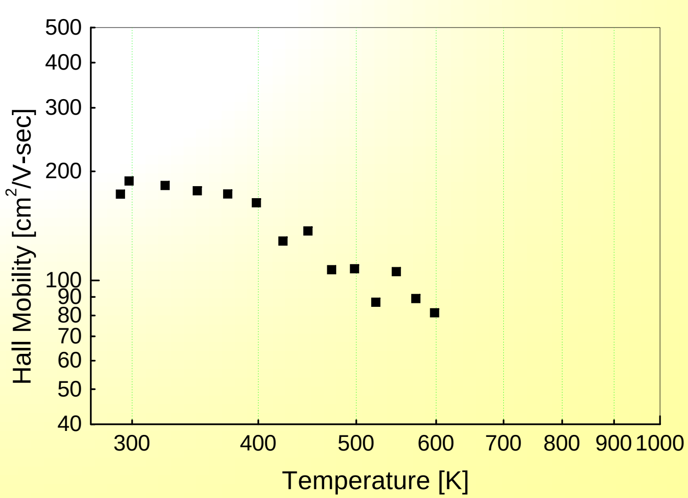




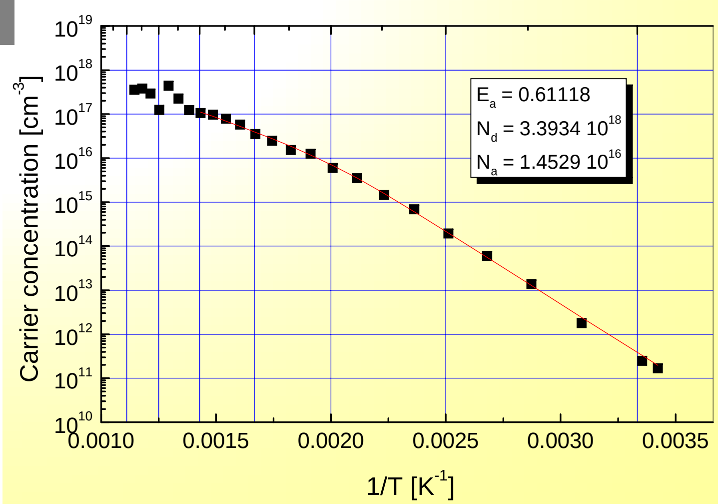
poly

300 ppm

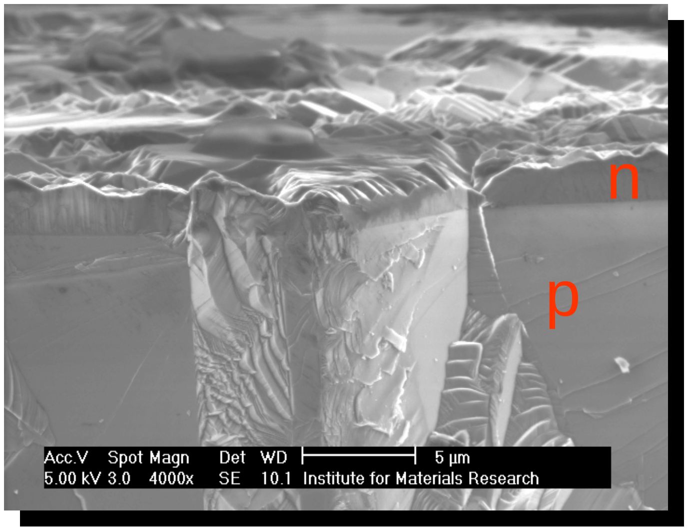
PH_3/CH_4



SC



Large area poly CVD diamond pn-junctions



Polished Si substrate

⇓

B-doped CVD layer (200 µm)

$N_A \sim 4\ 10^{18} cm^{-3}$

⇓

P- doped CVD layer (2 µm)

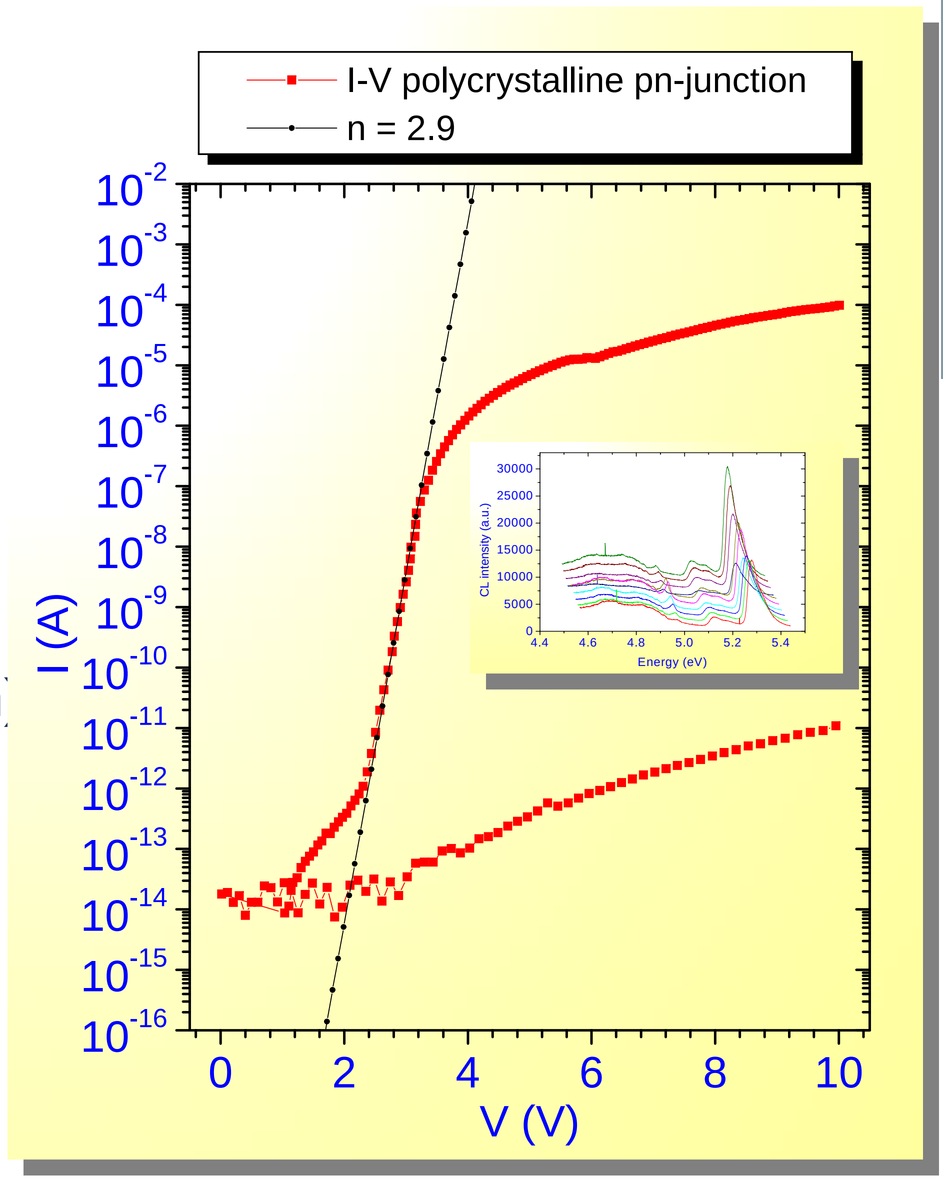
$N_D \sim 5\ 10^{18} cm^{-3}$

⇓

C/Ti/Au 1mm dots

⇓

I-V of diodes tested



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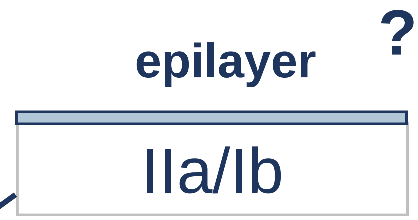
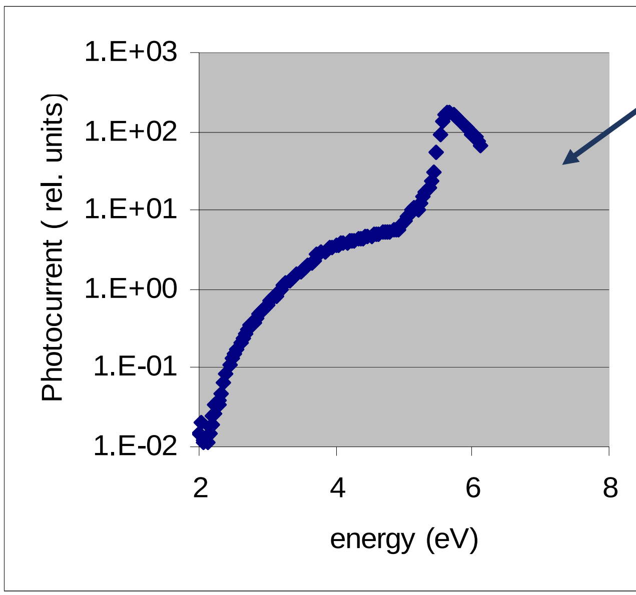
Lyra Detector design:

5mm SCD substrates
Photoresistors:





Sensitivity /rejection ratio optimisation

$\tau_{layer} > \tau_{substrate}$ (100psec)

↓

Undoped-> B-doping $10^{15}cm^{-3}$

1 µm litography: to limit the electric field in the substrate

Stable oxidised surface

Previous work on UV detectors:
Surface treatments on Poly CVD diamond
R. Jackman & P; Bergonzo:
Semiconductors and Semimetals 2004

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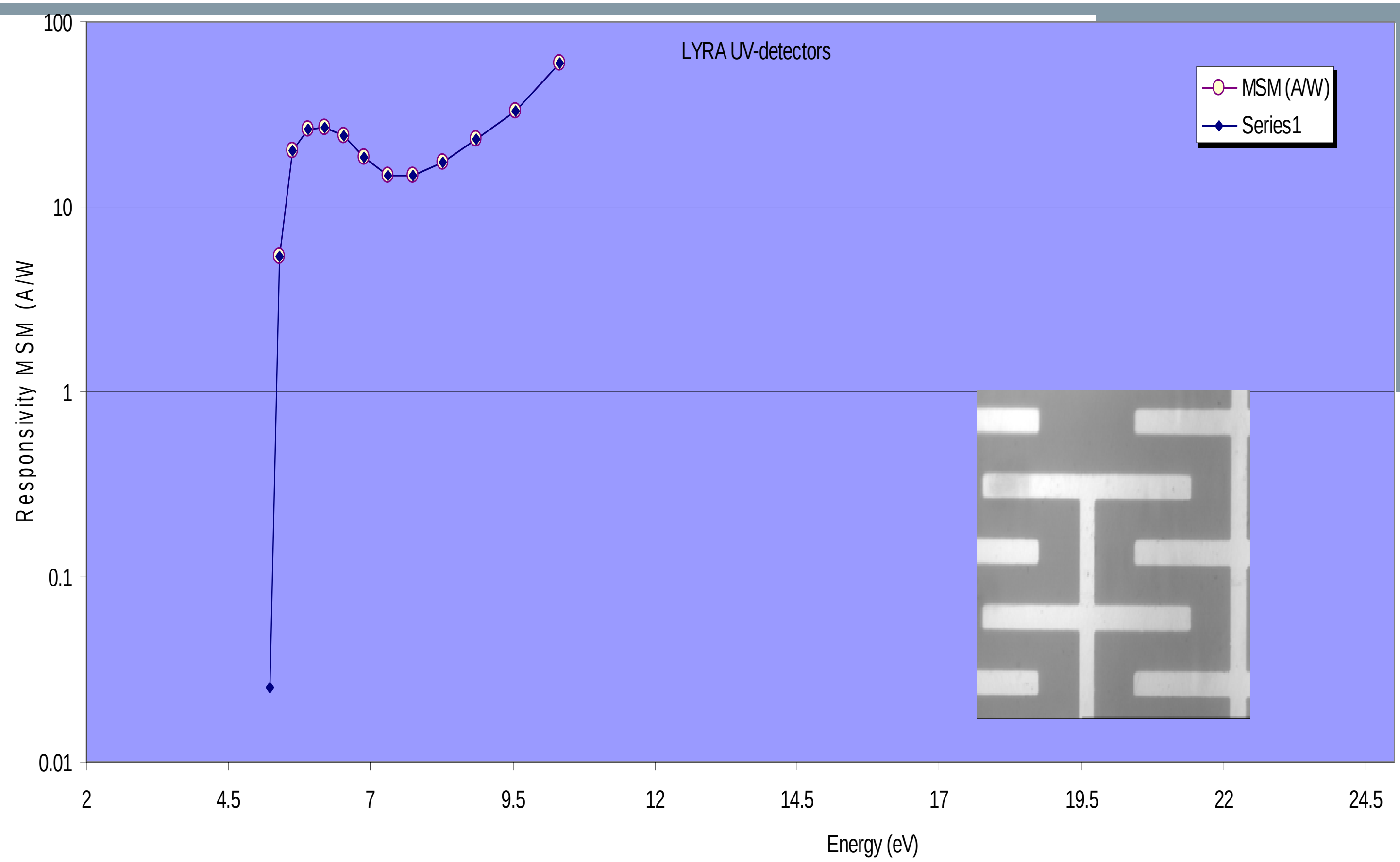
Synchrotron measurements: solar blindness, response time, S/N ratio



50 µm litogrpaphy

Pure S/N ratio (1-2 db at 1µW; 200 nm)

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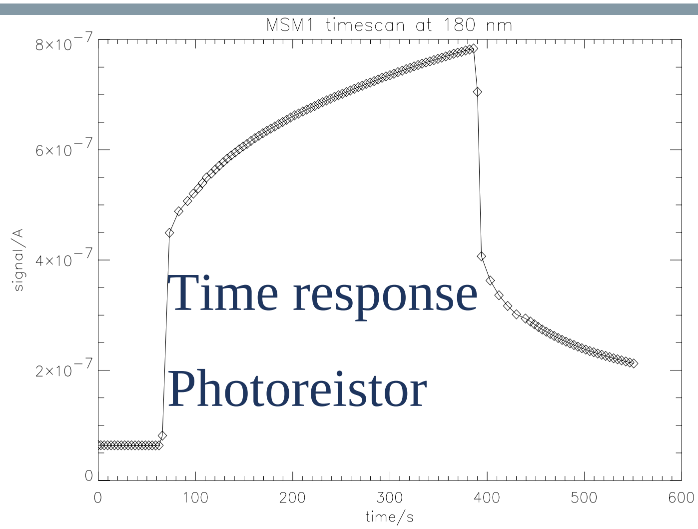
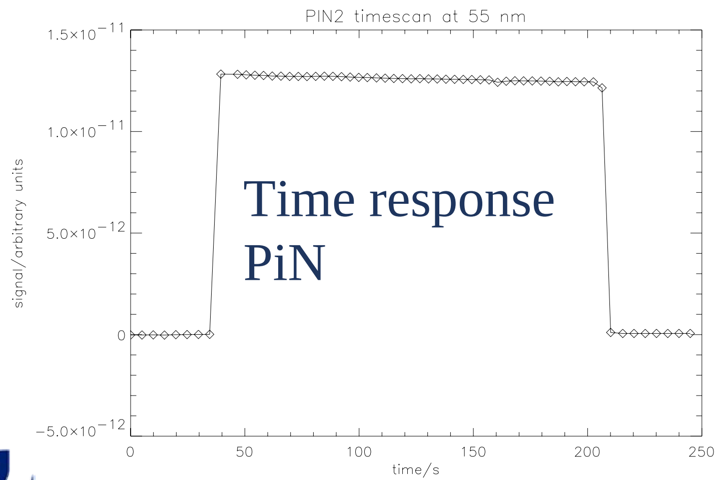
BESSY Measurements - synchrotron



Time response
Photoreistor

π– doping
High responsivity
Slow response
(traps modelling)
B 0.37eV,Dx 0.9eV, N1.7eV



Epi Layer optimisation
No B doping
Electrons ?
N, P… low incorporation
In (100)

Time response < 1 μsec

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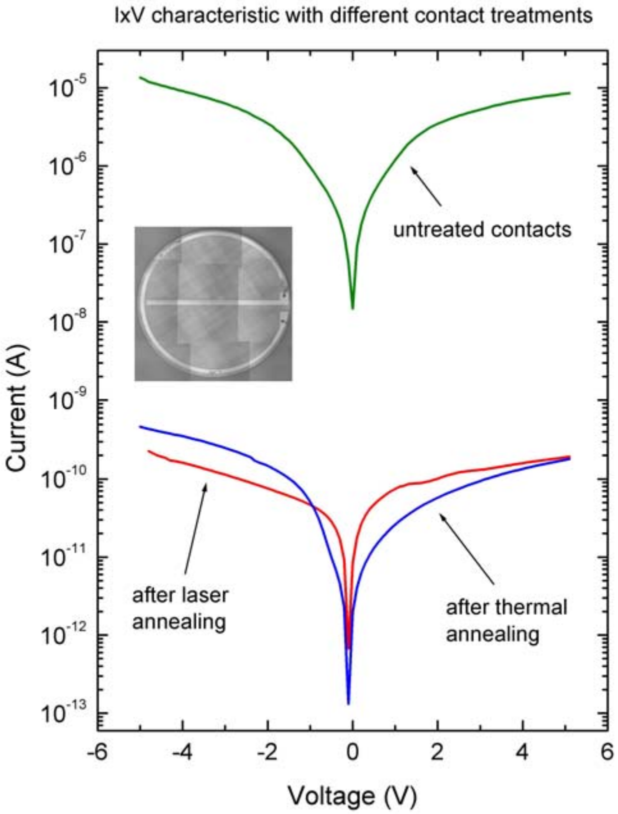
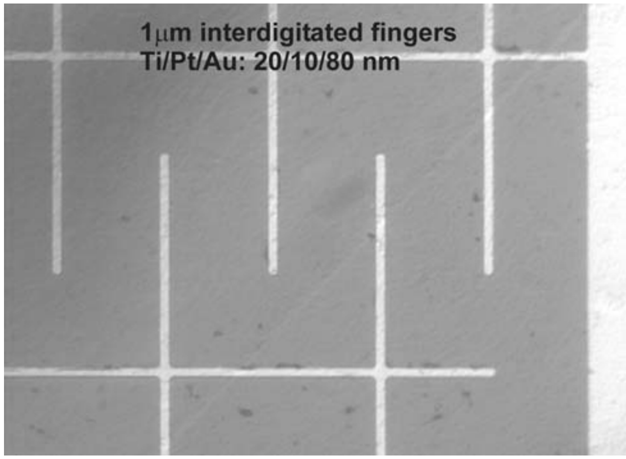
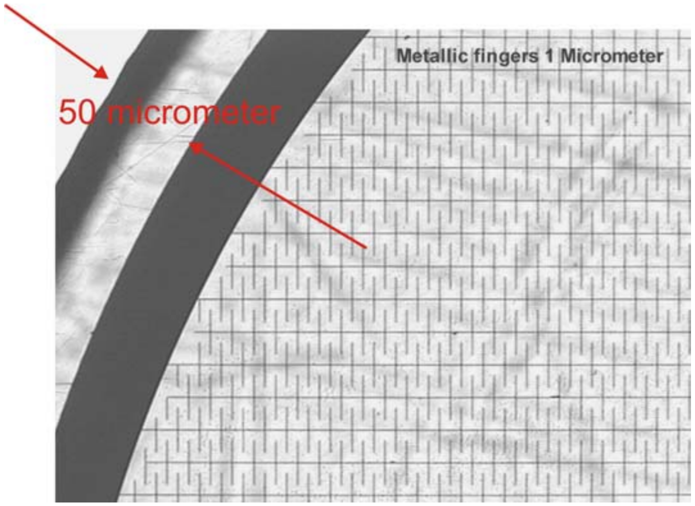
Photoresistor optimisation

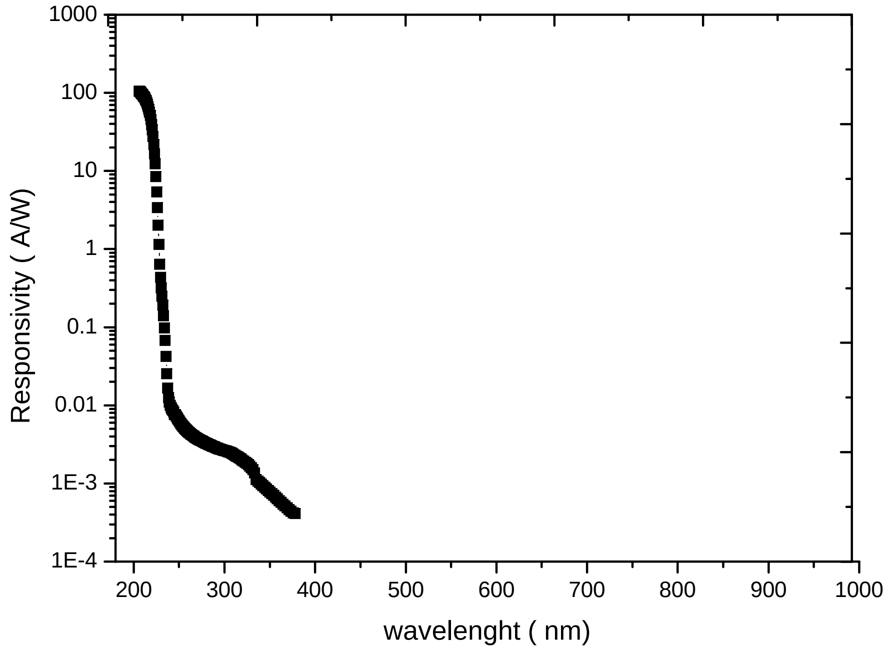


Photoresponse " Shubweg"
Optimisation $S = \mu\tau E$





Optimised photoresponse of epitaxial CVD diamond photoresistor detector (5mm)



Response time < 10 μsec
5V; dark current < 5pA
1 μm litography

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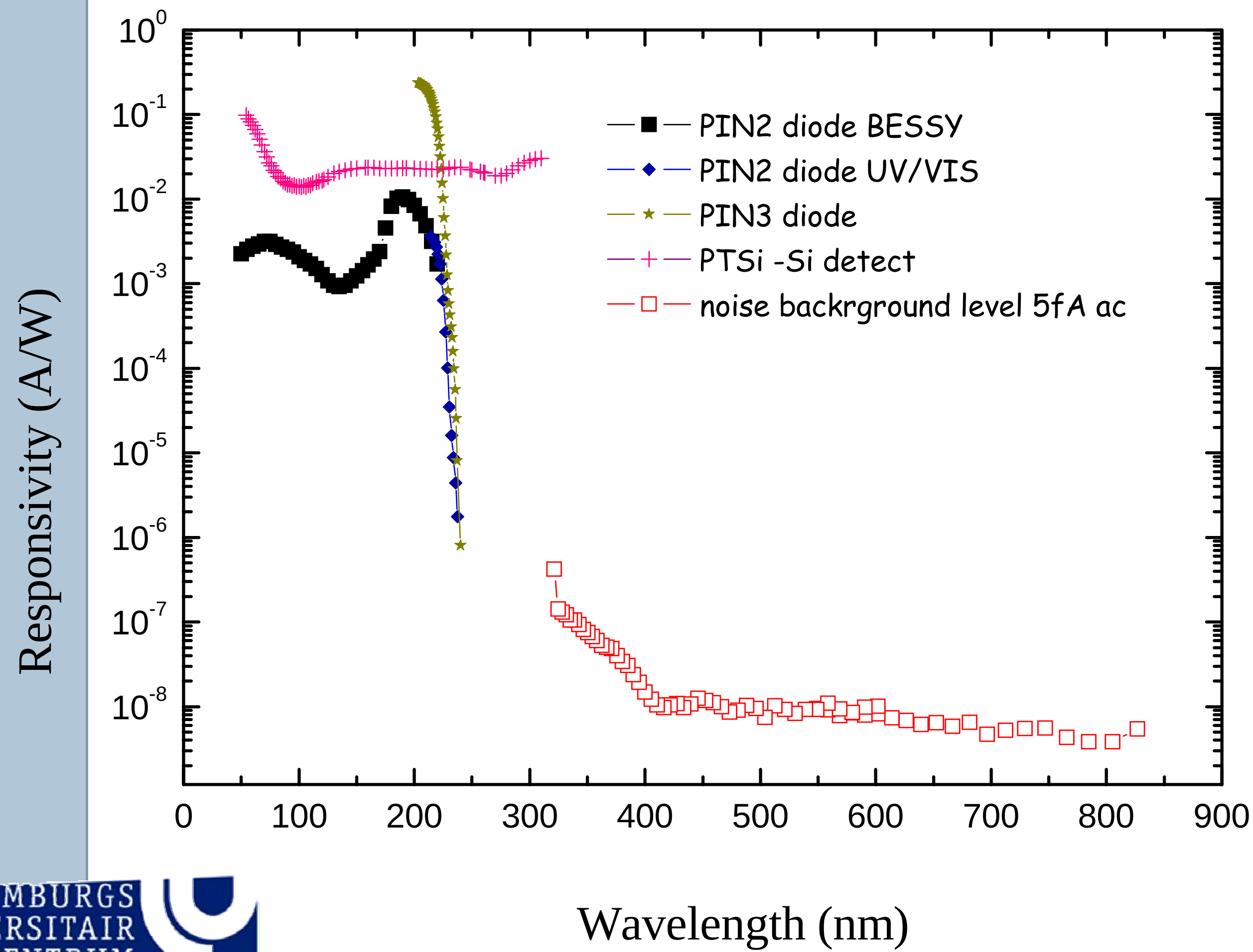
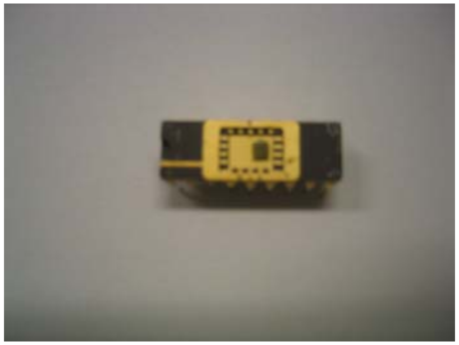
Optimisation of photoresponse of epitaxial (111) PiN CVD diamond detector (5mm)

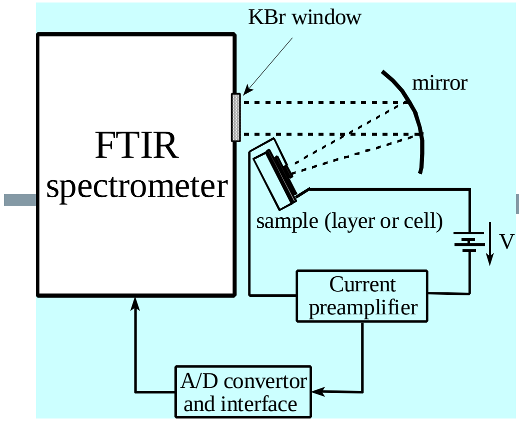


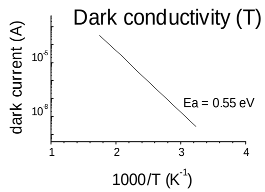


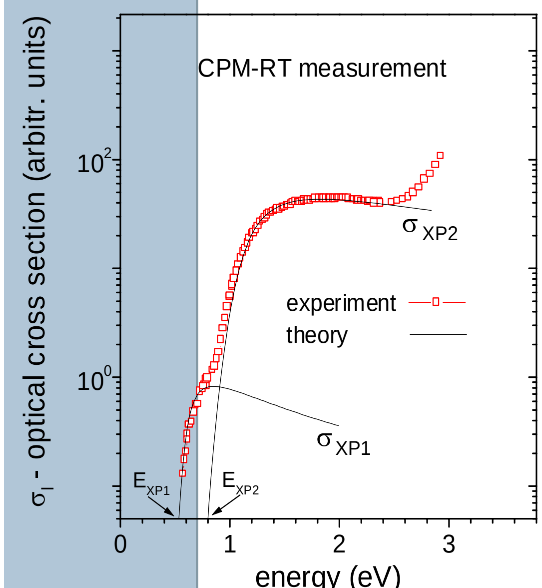
Outline

1. Intruduction: detectors onboard ESA Satellite Proba II.
2. Growth of epitaxail n-type CVD diamond
    - Growth
    - Mobilities
    - Electronic structure
3. Growth of polycrystalline n-type CVD diamond
    - Preferred orientation
    - Mobility (Hall)
    - CL, electronic structure
4. Devices
    - Epitaxial and polycrystalline diodes: UV “solar blind” sensors, …

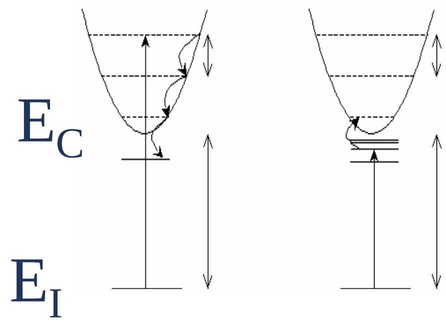
1.2 Fourier Transform Photocurrent Spectroscopy (FTPS)

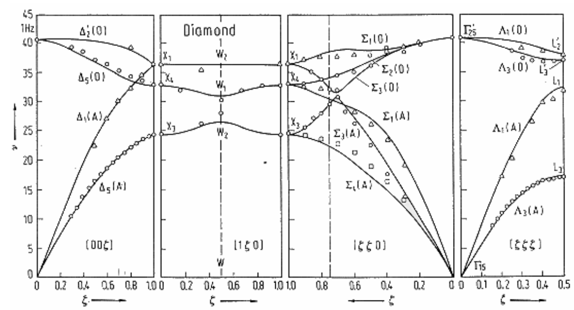


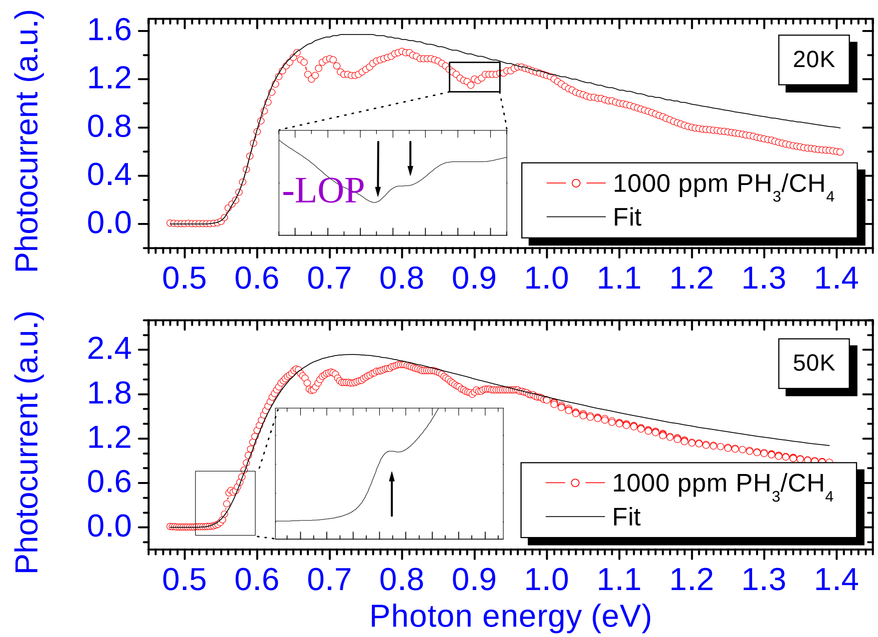




$$\sigma(E) = A\int_{-\infty}^{+\infty} \frac{\sqrt{\varepsilon - E_I}}{\varepsilon\,(\varepsilon - B)^b}\,\frac{\exp\left(\frac{-(E-\varepsilon)^2}{2w^2}\right)}{\sqrt{2\pi w^2}}\,d\varepsilon$$





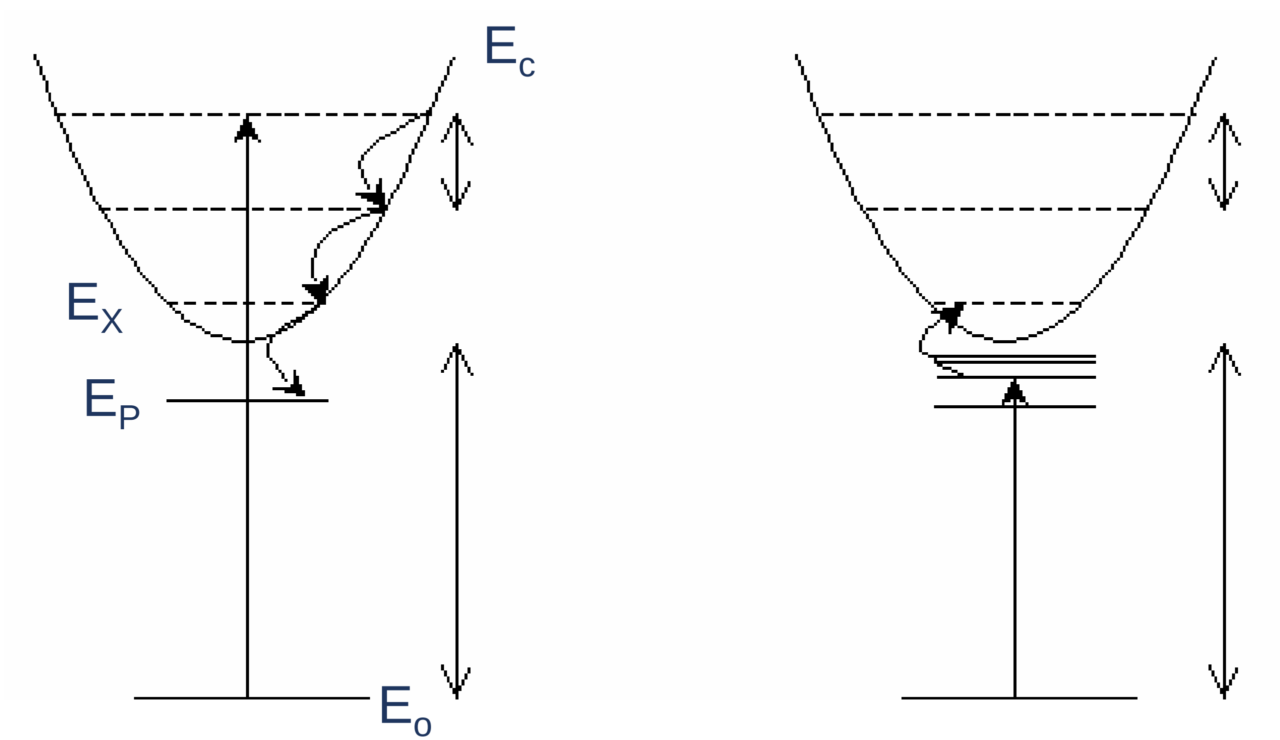


P in diamond: 0.60 eV

Nesladek et al, Phys. Rev B 1999

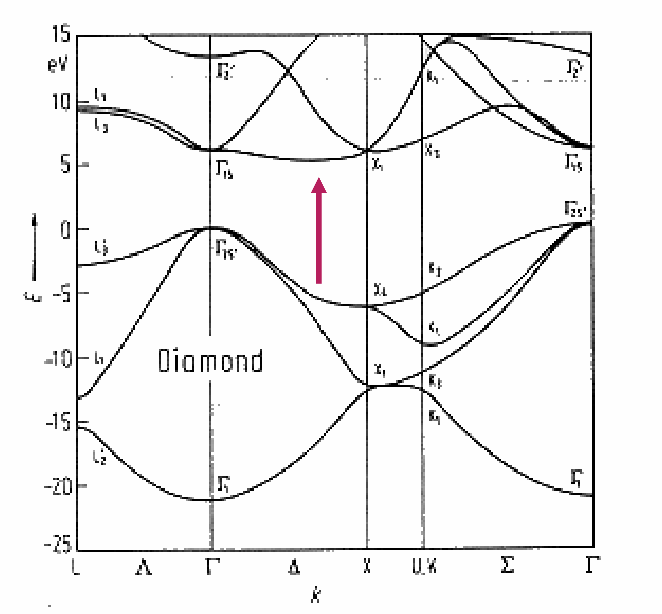
The electronic structure of P (PC – PTIS)

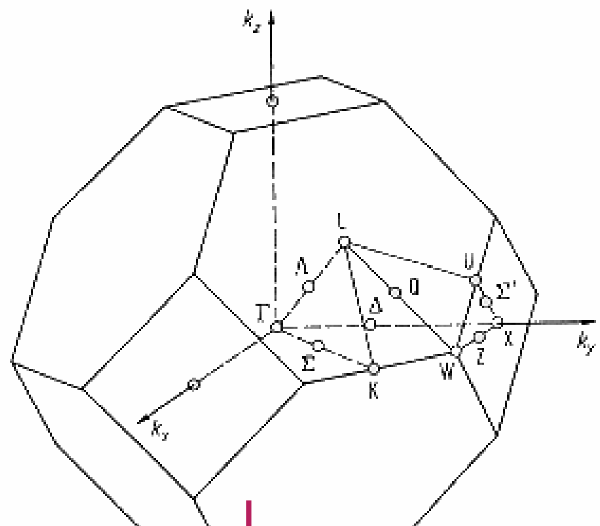
- Oscillatory PC and PTIS maxima provide complementary information about the excited states of phosphorous



$$E_P = E_X - n\,LO$$

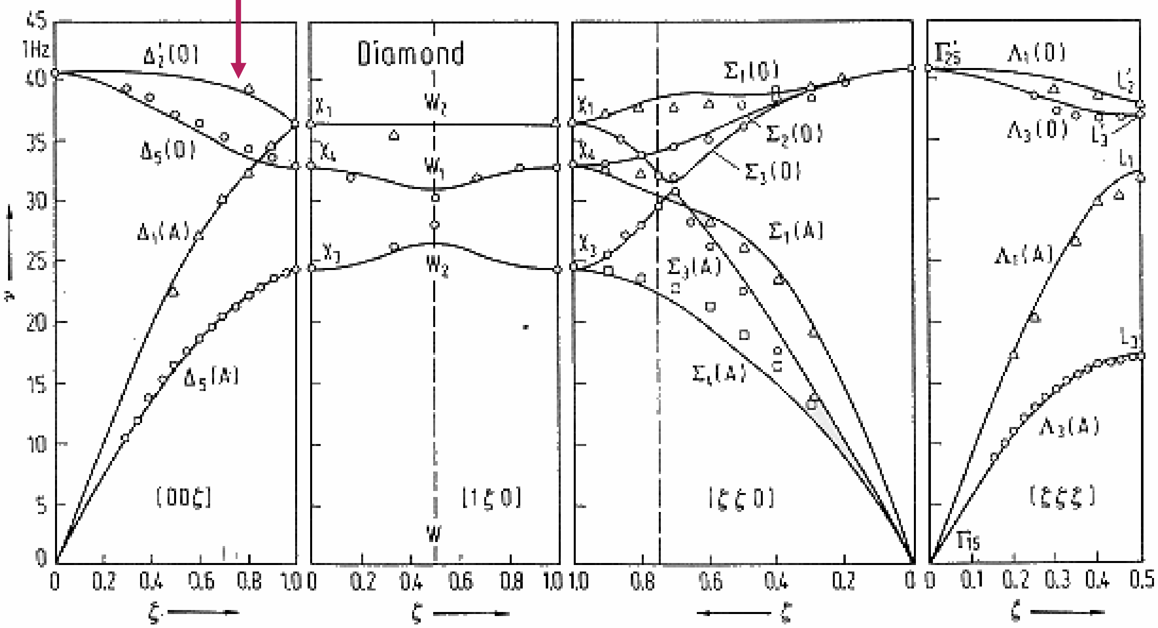
Bandstructure and phonon dispersion curves





CB minimum [100]

Δ-axis **k** = 0.75 **k**$_0$



LO = 155 meV

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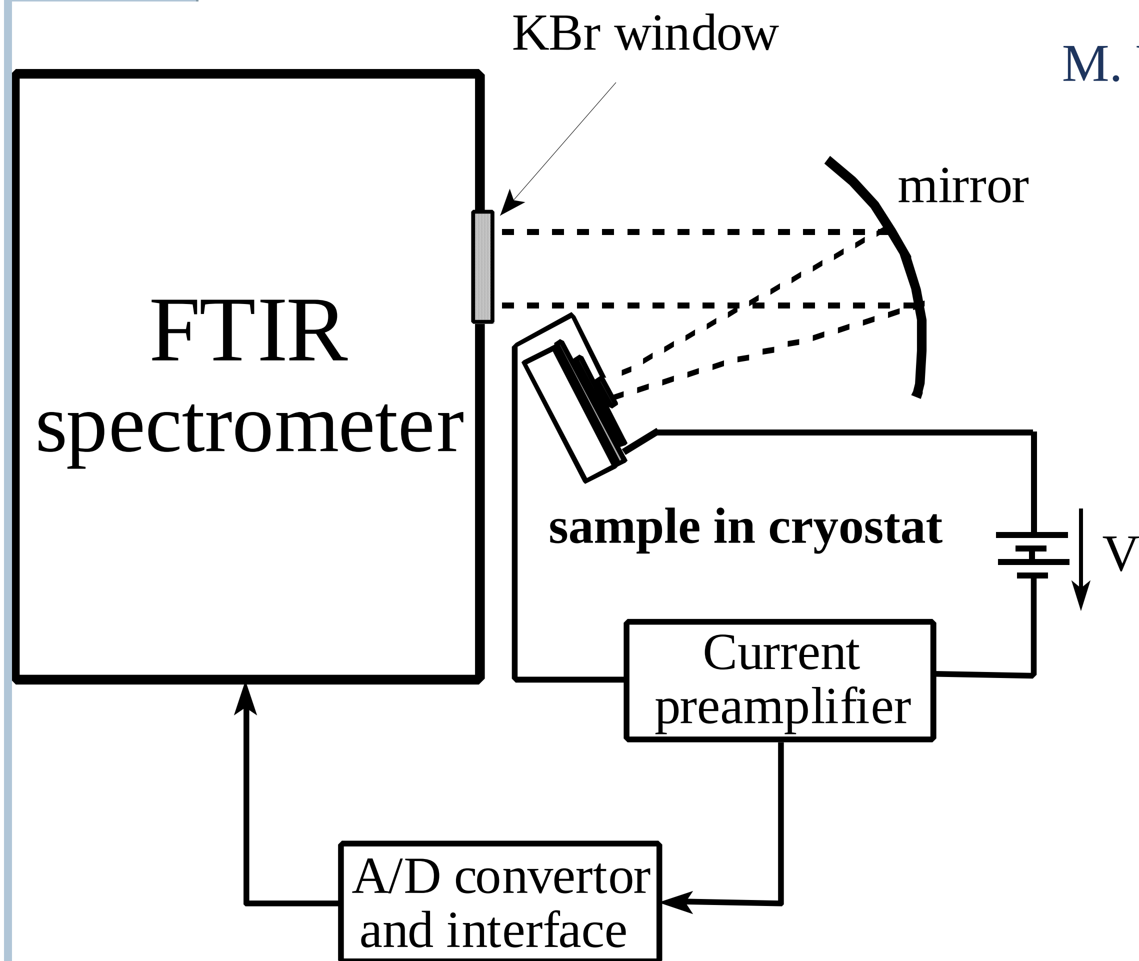
Fourier Transform Photocurrent Spectroscopy

M. Vaněček *et al.*, APL **80** (2002) 719



- FTIR spectrometer
- External beam output
- External detector
- Quartz, CaF_2 and KBr beamsplitters (IR – VIS)
- Stable voltage source
- Sample in LHe-LN cryostat (77K – 500K)

Normalized FTPS signal (a.u.):
signal from the sample normalized by the signal from spectrally independent pyroelectric detector.

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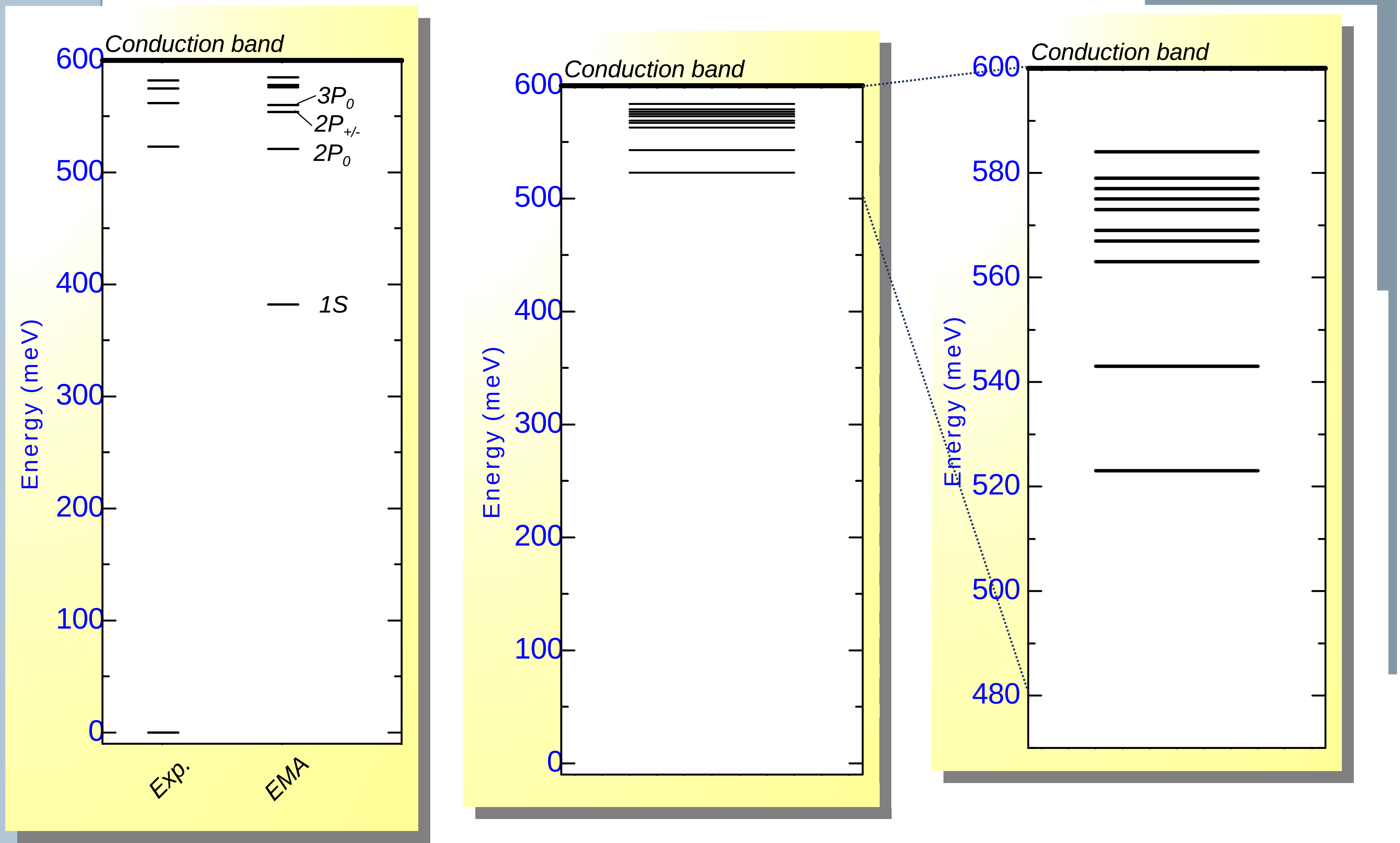
The electronic finestructure of P



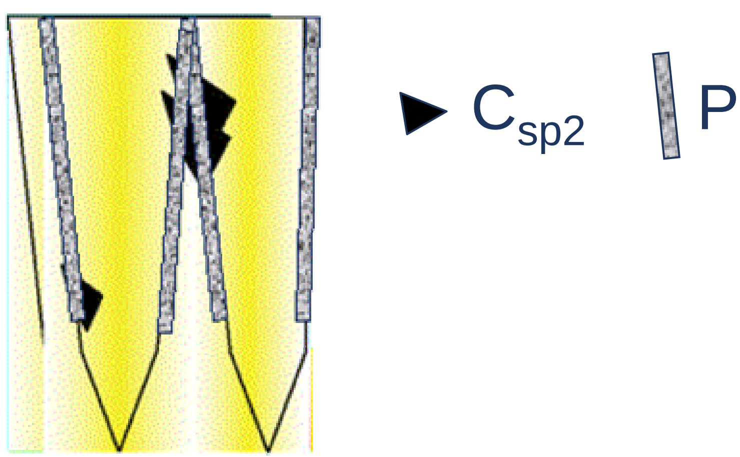
Gheeraert *et al.*, DRM **10** (2001) 444

Poster 5.5.9

Growth of polycrystalline n-type diamond

- Motivation:
  - Large area growth and processing of n-type diamond
  - Polycrystalline pn junctions
  - Achieve RT exciton emission on polycrystalline pn junctions
- Problems: Grain boundaries and P-incorporation

Growth surface



Nucleation surface

- Proces parameters

P: 800W, p: 100 Torr

T: 850 – 900 °C

PH_3/CH_4 : 100 – 500 ppm