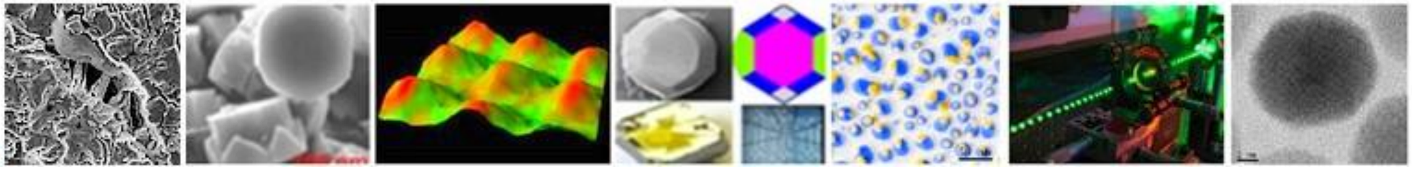


LABEX SEAM

Ingénierie de la synthèse de monocristaux de diamant CVD pour les applications à base de centres NV

J. Achard
LSPM-CNRS, Université Paris 13

Colloque Labex SEAM – lundi 12 novembre 2018

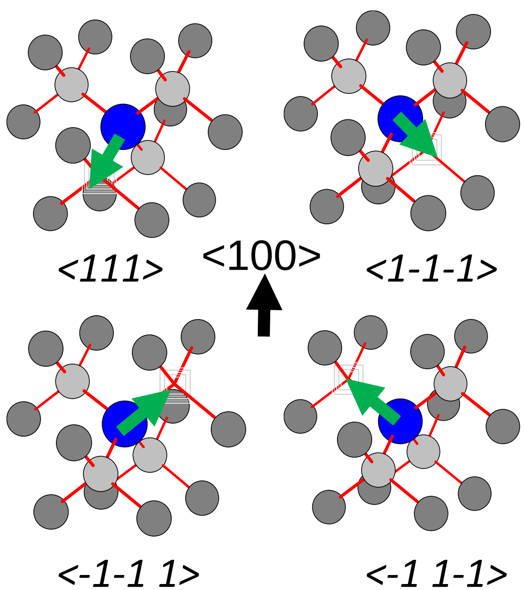
Nitrogen-Vacancy centres in diamond

pink diamonds

W. Wang Gems & Gemmology 2010

One of the many optical defects
Rare in natural diamonds
Very common in CVD diamonds

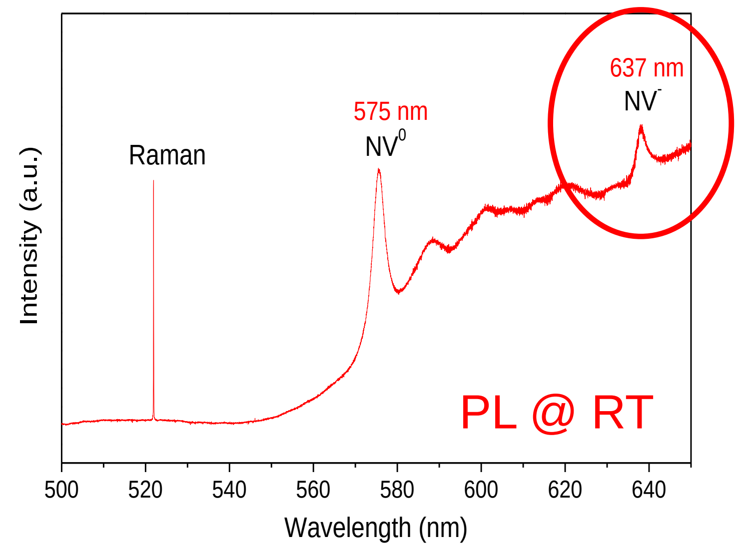
N-V bond oriented along <111> → **4 possible orientations**



2 known charge states, neutral and negative

ZPL @ 575 nm

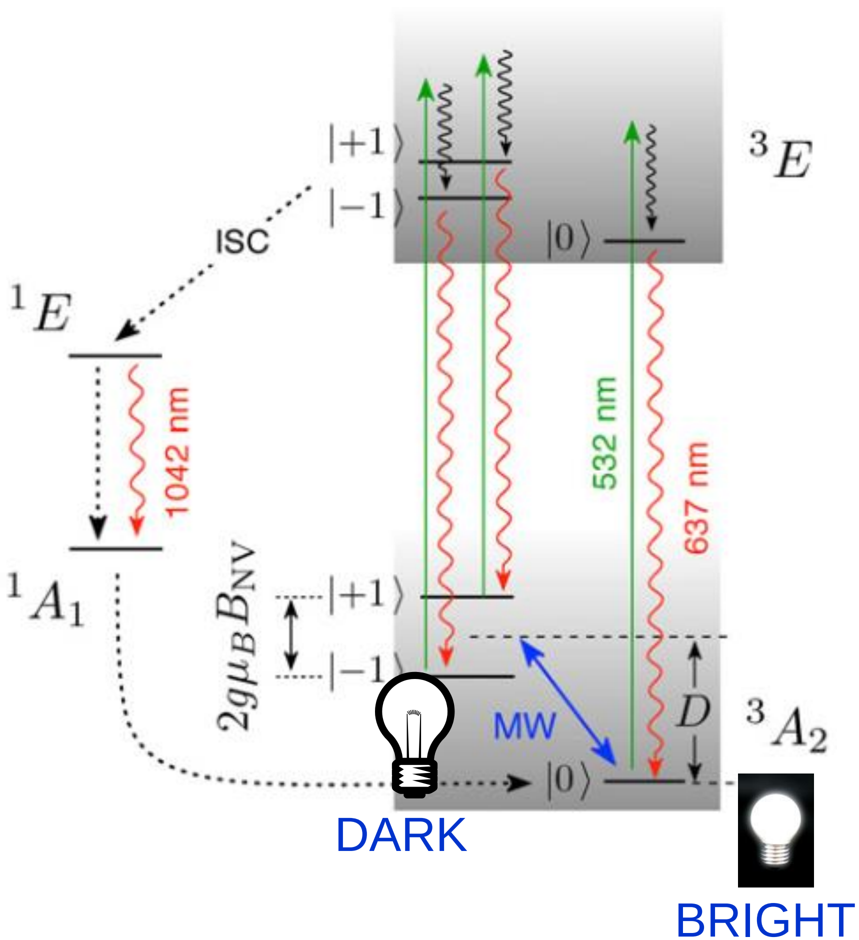
ZPL @ 637 nm



$N_s + NV^0 \rightarrow NV^- + N_s^+$

Properties of NV centres

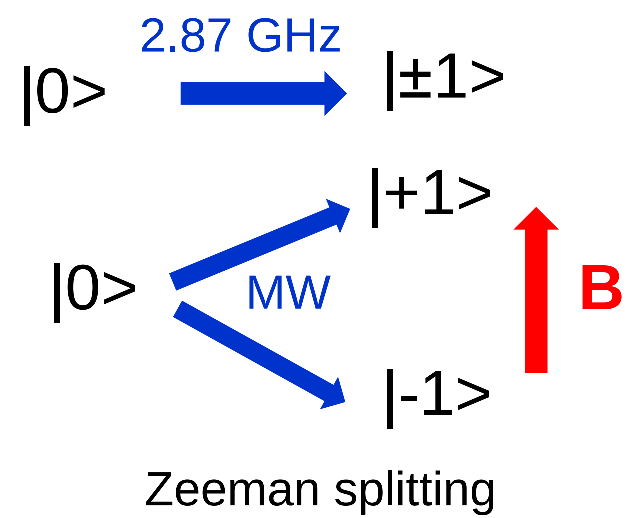
Electronic structure of the NV$^-$ centre



Pumping with a 532 nm laser

→ **polarisation in the |0> state**

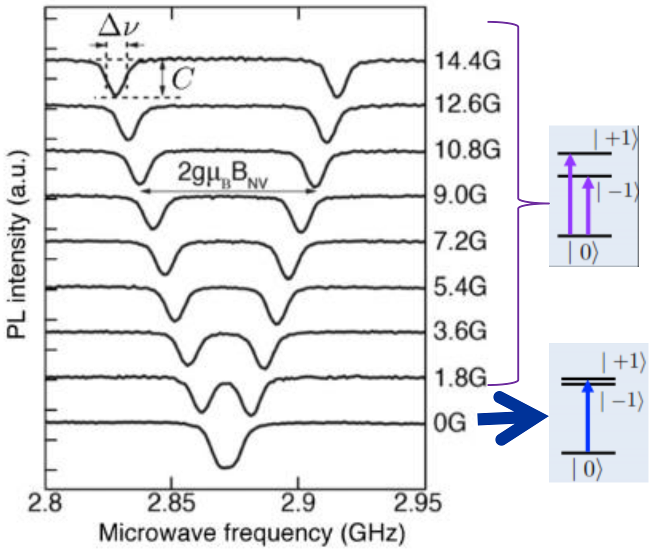
Initialising and reading the spin state at room temperature



Rondin et al. Reports on Progress in Physics 77 (2014) 056503

Properties of NV centres

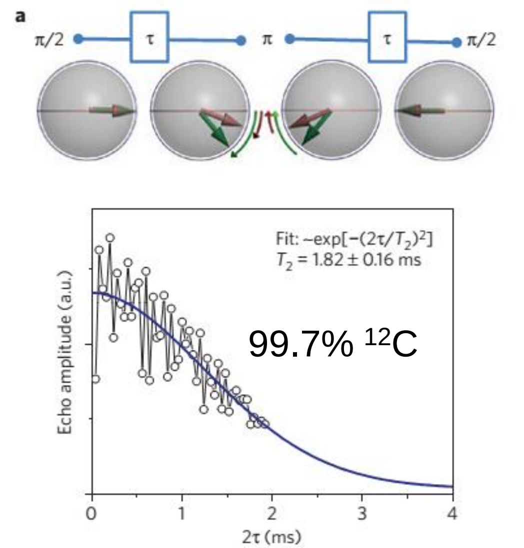
Optically Detected Magnetic Resonance



Gruber et al. Science 276, 2012 (1997)

Extreme sensitivity to
B field

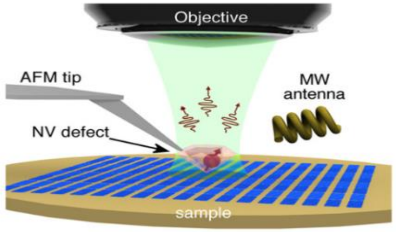
Spin Echo



Balasubramanian et al. Nature Materials 8, 383 (2009)

Coherence time up to
2 ms @RT

Applications for NV centres

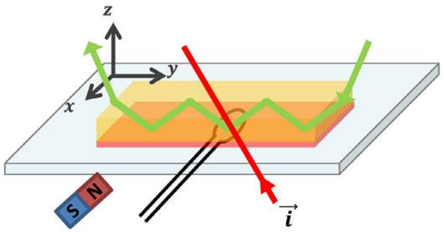


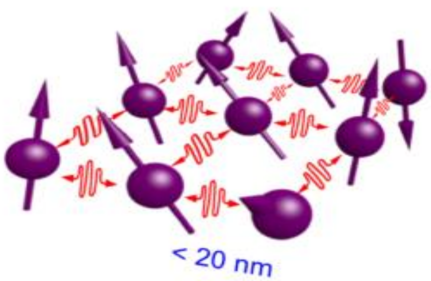
Magnetic probes with nanoscale resolution

L. Rondin APL 100, 153118 (2012)

Wide field magnetic imaging

M. Chipaux et al. The European Physical Journal D, 69 (2015) 166.



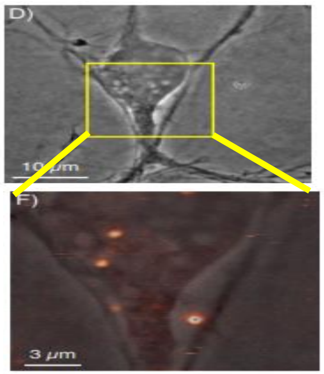


Arrays of NVs for quantum information processing and quantum cryptography

M. Loncar MRS Bulletin 38 (2013) 44

Biolabelling with bright emitters

M.P. Adam, PhD Thesis ENS Cachan 2013

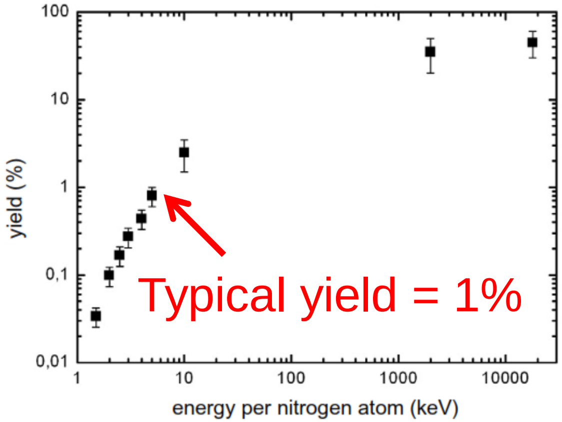


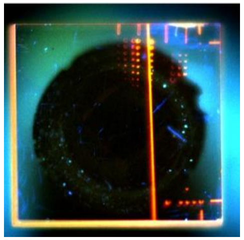
Creating NVs in CVD diamond

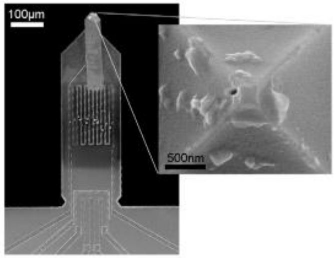
Implantation and annealing

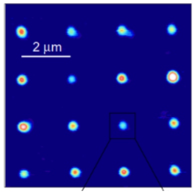
VS

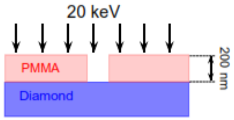
In-situ doping during growth







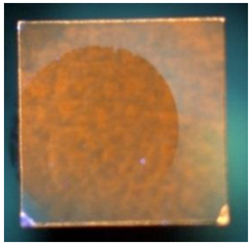




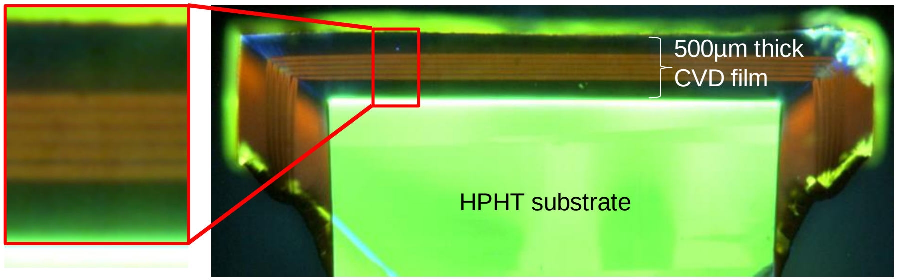
Pierced -AFM tip or etched PMMA

Low yield and damage (shorter T_2) but accurate positionning possible

Pezzagna et al. New Journal of Physics 13, 035024 (2011).



10 ppm N_2 → 55 ppb N_s → 0.2 ppb NV^-

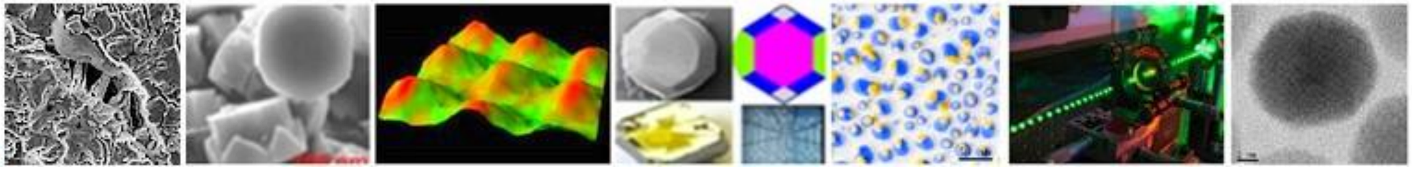


Cross section luminescence image

Stacking of layers with high NV doping

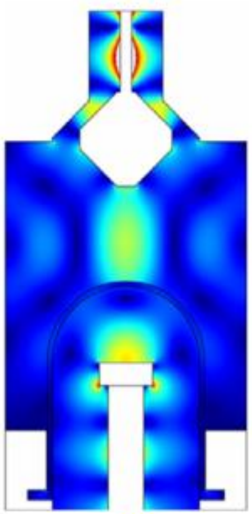
Moderate yield and longer T_2 but localization difficult

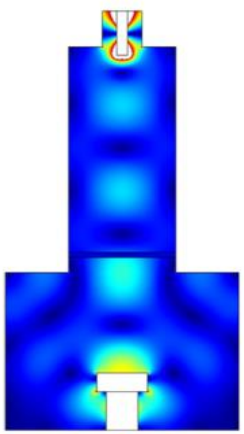
A. Tallaire et al., Diam. & Relat. Mat. 15, 1700-1707 (2006)

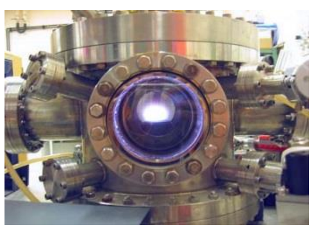


The CVD technique for producing single crystal diamond films with NVs

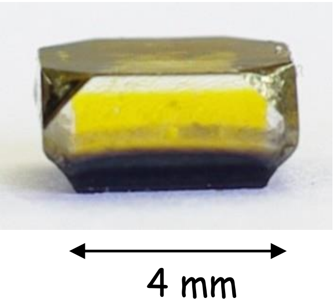
CVD growth of diamond: a KEY TECHNOLOGY







MW plasma assisted CVD
Homoepitaxial growth on HPHT substrate
High power densities (>100 W/cm^{-3})
H_2/CH_4 (95/5)
800-1000°C

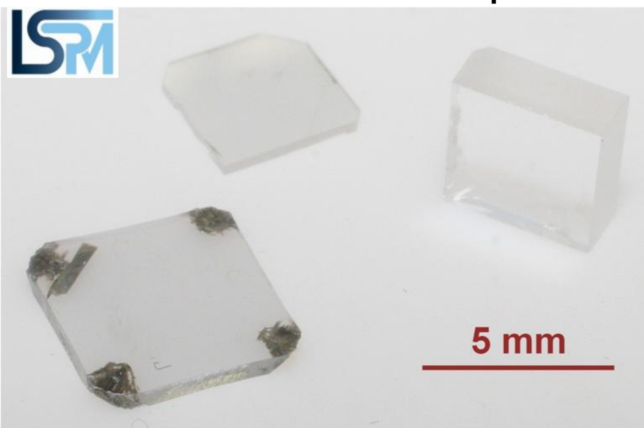


Growth rates 1-10 µm/h

CVD growth of diamond: a KEY TECHNOLOGY

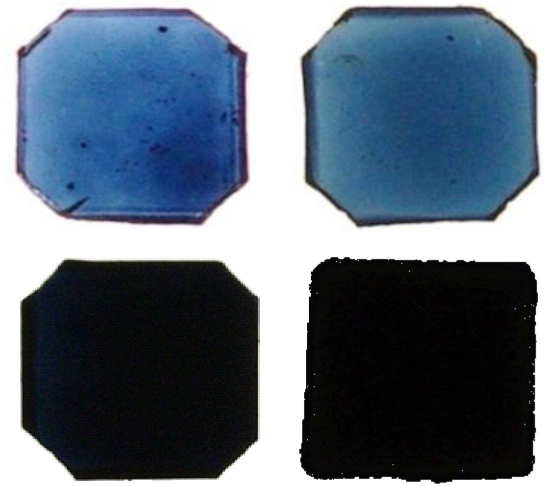
A fairly mature technology

Millimeter-thick ultra-pure



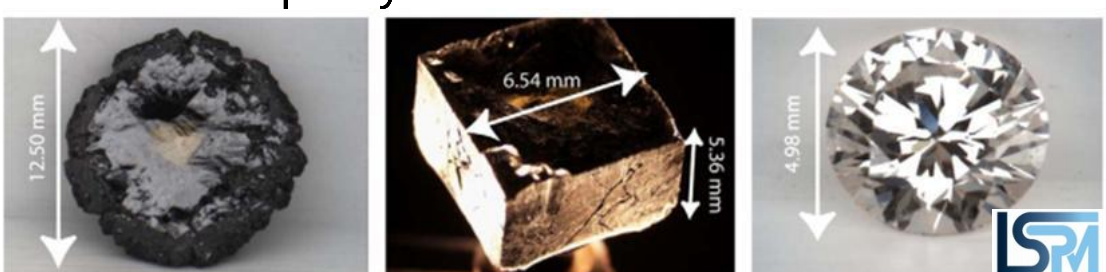
Tallaire et al., Comptes Rendus Physique 14, 169-184 (2013).

Boron doped CVD substrates



J. Achard et al., Phys. Stat. Sol. (a), 209, 1651-1658 (2012).

Gem-quality material



B. Willems et al. Diam. & Relat. Mat. 41, 25-33 (2014)

HRDAntwerp
Institute of Gemmology

Challenges for QT material synthesis

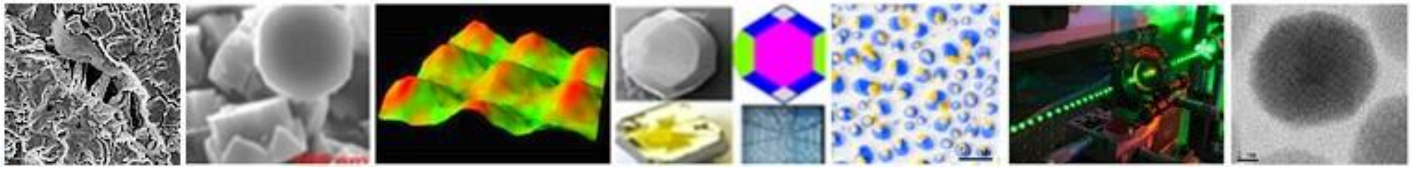
1. Controlling **the environment of NV centres and their density** for achieving long coherence times (isotopic purity, impurities of N, B etc, extended defects…)

2. Controlling **the orientation of NV centres** (among the 4 possible…)

3. Controlling **the spatial position of NV centres** (arrays of NV, delta-doped layers, NVs in photonic cavities…) and bringing **NVs close to the surface** (stable charge state)

4. Controlling **the dimensions and shape of the diamond matrix** (membranes, pilars, thick bulk plates)

VERY HIGH REQUIREMENTS FOR THE PACVD TECHNIQUE !

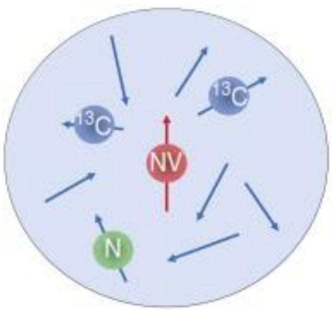


1. Controlling NVs environment and density

Isotopic purity control

$$\frac{1}{T_2} \simeq \left(\frac{1}{T_2}\right)_{^{13}\text{C flip-flop}} + \left(\frac{1}{T_2}\right)_{\text{nitrogen impurity}} + \left(\frac{1}{T_2}\right)_{\text{paramag. defect}} + \left(\frac{1}{T_2}\right)_{\text{spin-lattice relaxation}}$$

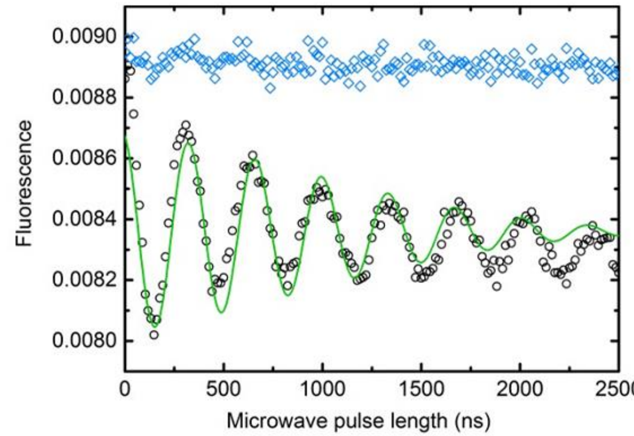
Sensitive to spin environment

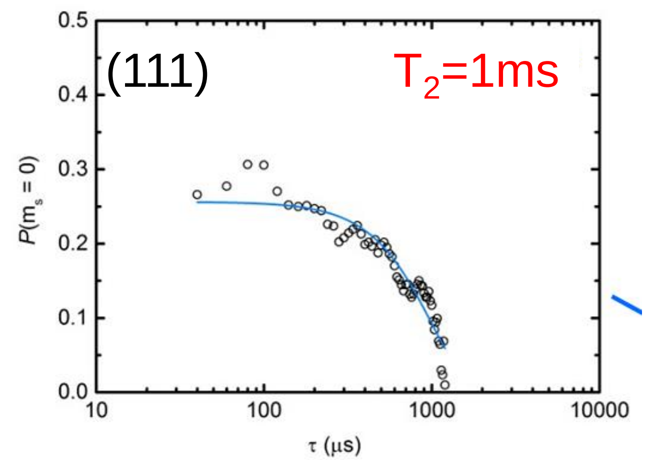


High purity and isotopically pure → up to several ms long

N. Bar-Gill et al., Nat Commun 3, 858 (2012).

$C_{nat}/^{12}C$ stack on (111) grown with ^{12}C CH_4 cylinder



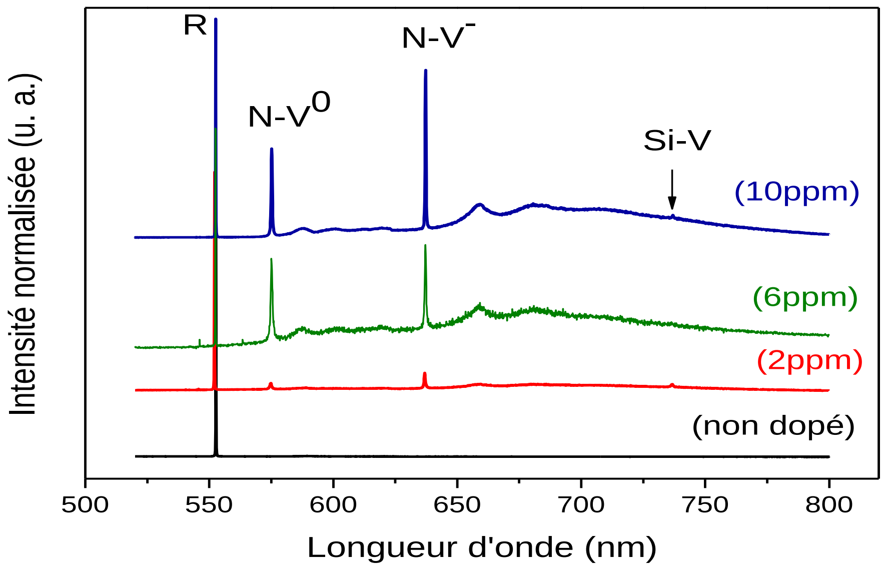


(Collaboration Basel University)

Controlling NV density

1. Single NV centers for sensors with nanoscale accuracy

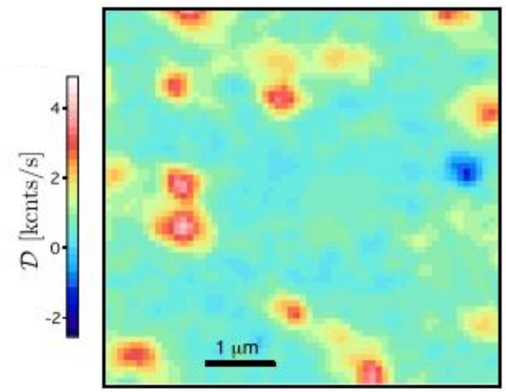
Control of doping by addition of N_2

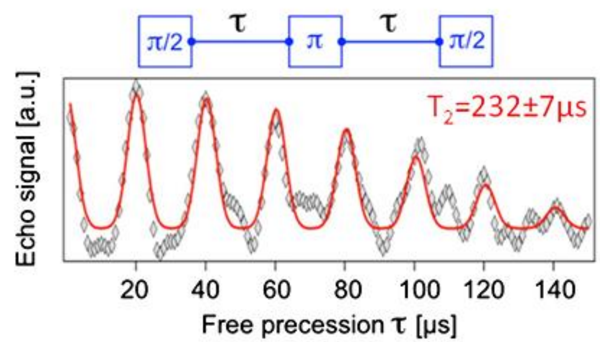


Low amounts of N_2 (0-10ppm)
Strong temperature dependence of N incorporation

Isolated NV centers obtained

0.01 ppb NV^-





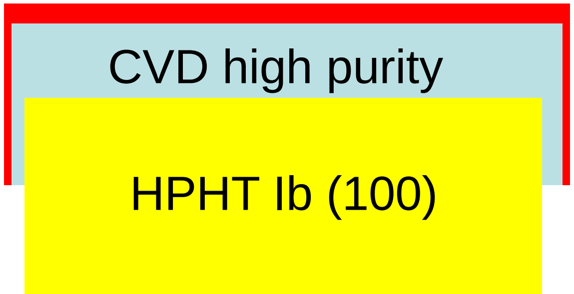
Collab. ENS Cachan/LAC-CNRS

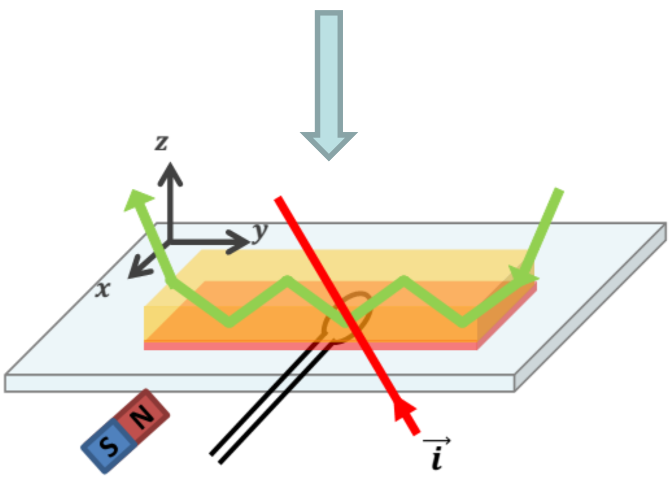
Controlling NV density

2. Creating ensembles of NV centers with high density

Magnetic sensivity increases with $(N_{NV})^{1/2}$

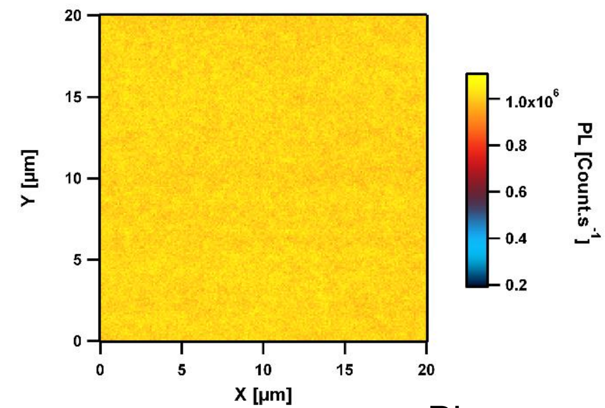
High N-doped CVD





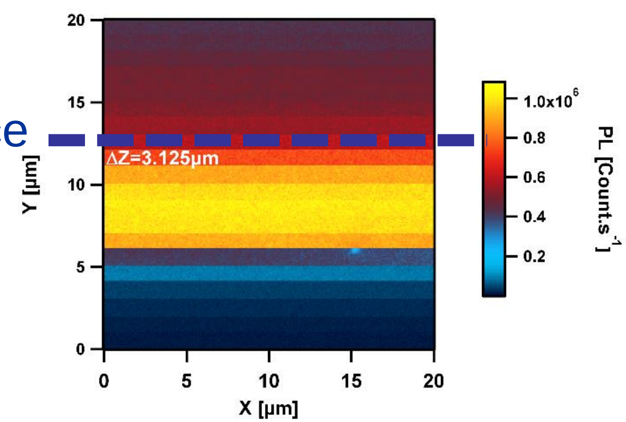
10 ppb NV^-

PL top view



PL cross-section

surface



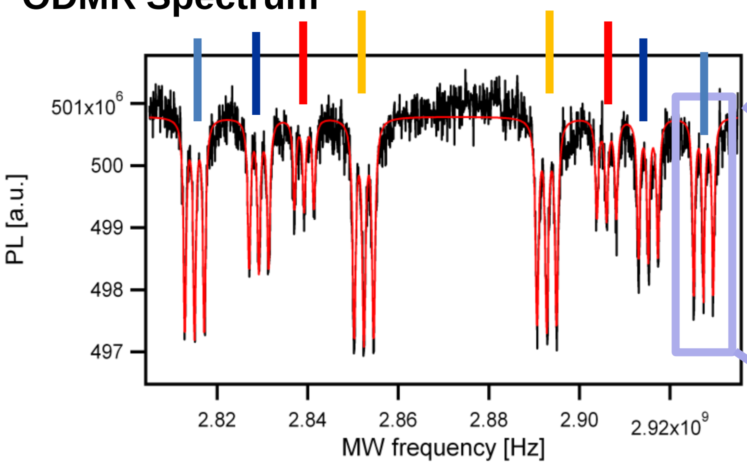
Collaboration Thales

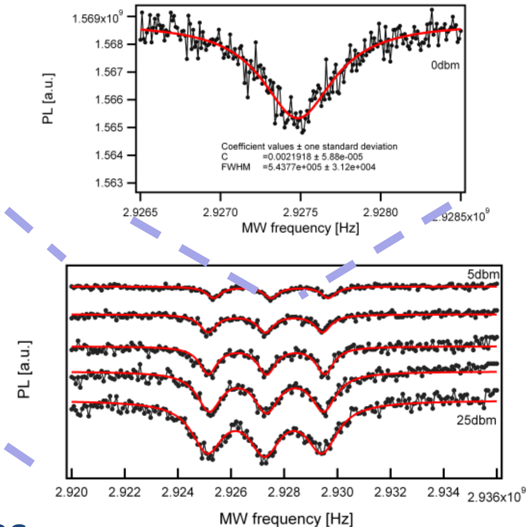
M. Chipaux et al. The European Physical Journal D, 69 (2015) 166.

Controlling NV density

2. Creating ensembles of NV centers with high density

ODMR Spectrum

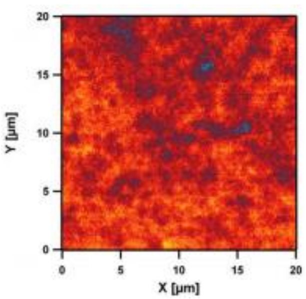




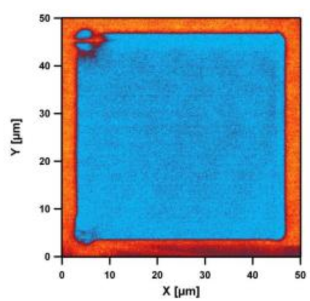
4 pairs of resonances = **4 orientations**

- Observation of the triplet due to nuclear spin of N^{14}
- FWHM around 500 kHz (Good coherence time expected)

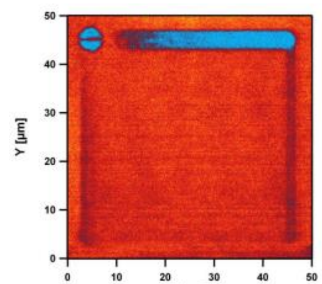
ISSUE OF PHOTOSTABILITY



Reference

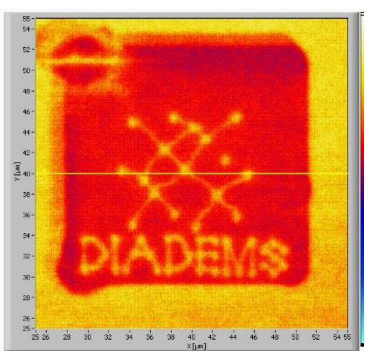


Photobleaching by laser scan 5mW power



Erasing by laser scan 500nW power

Can be used for writing!



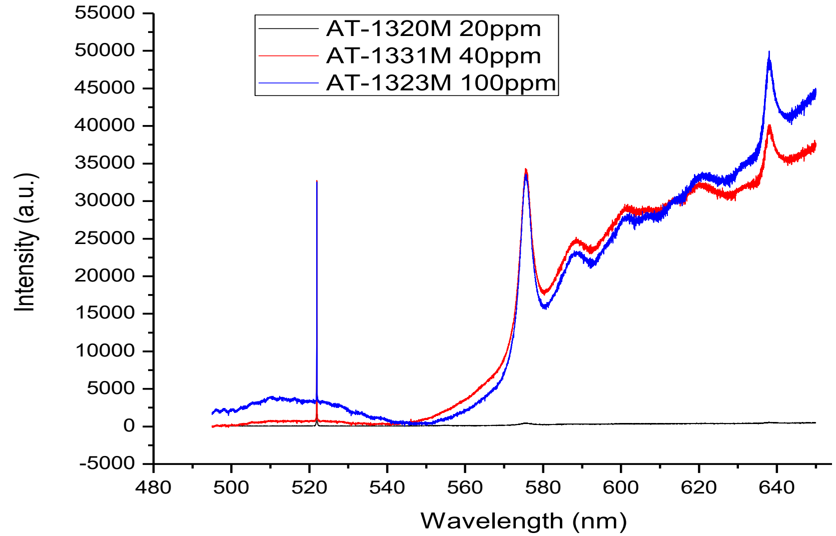
www.diadems.eu

Controlling NV density

Further increasing NV doping?

N_2= 20ppm 40ppm 100ppm

Saturation/quenching of NV PL

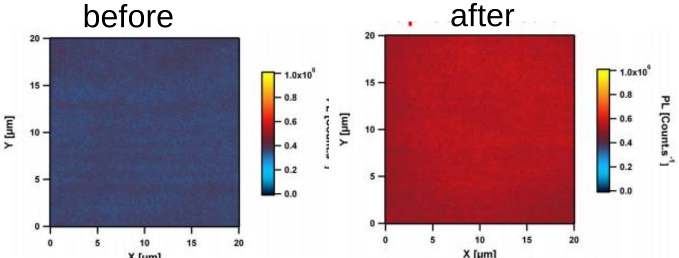


Use of post-treatments: implantation

Creating vacancies by irradiation and NVs by annealing

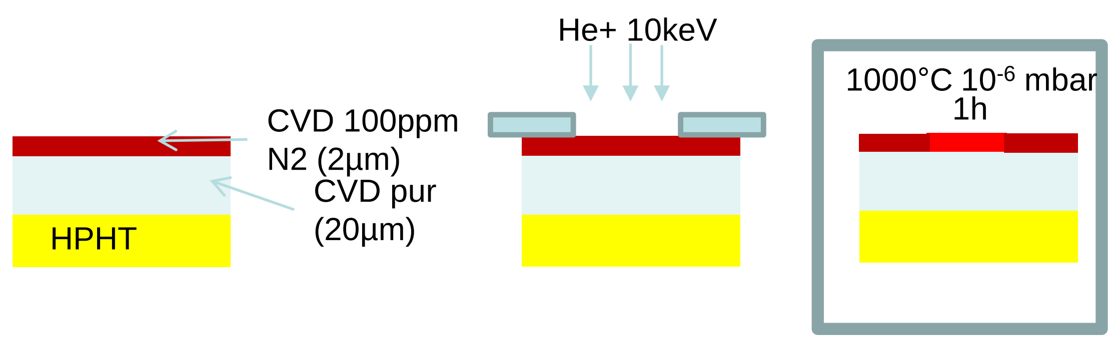
Electron implantation 5 MeV + anneal

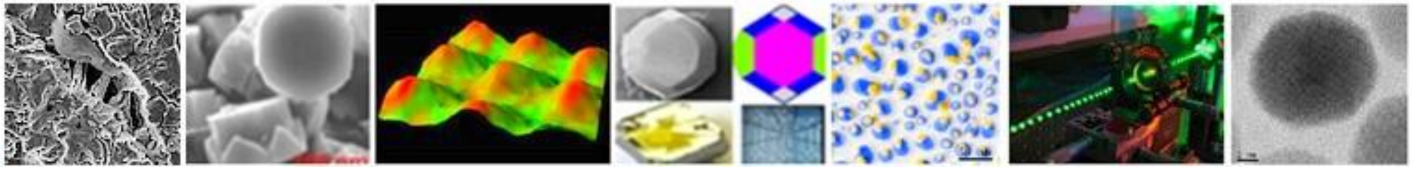
before after



I_{photon} = 450 kct.s^{-1}

I_{photon} = 550 kct.s^{-1}



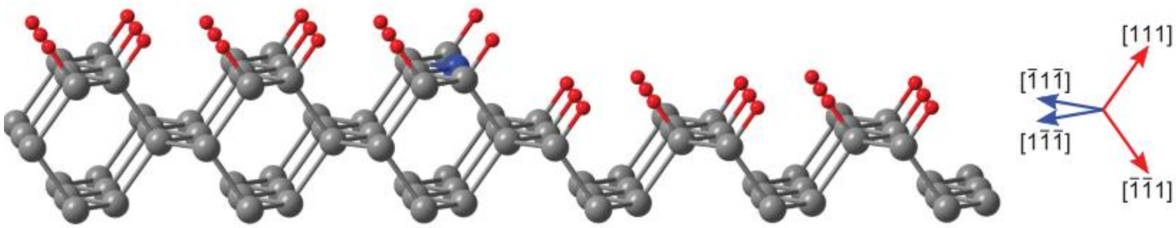


2. Controlling NVs orientation

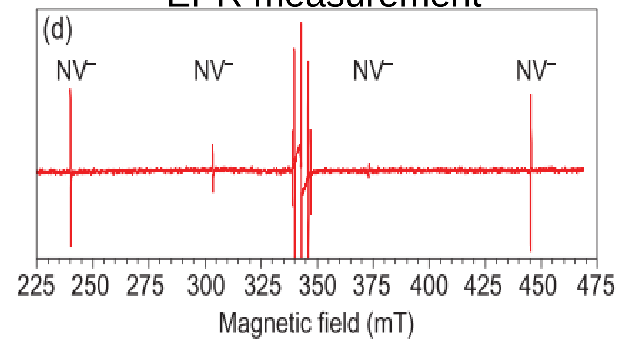
2. Controlling NVs orientation

Growth on (110) orientation

(110)



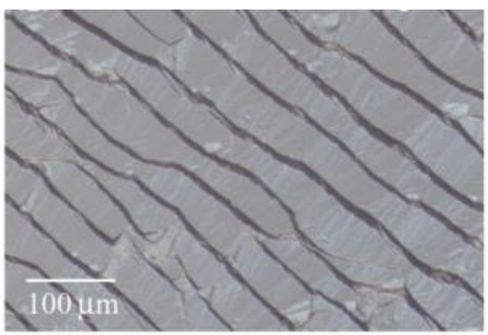
EPR measurement

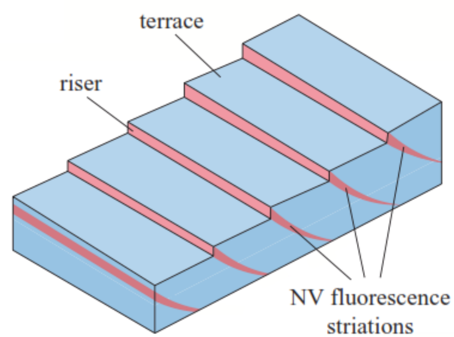


(110)-grown CVD diamond→ 50% preferential orientation

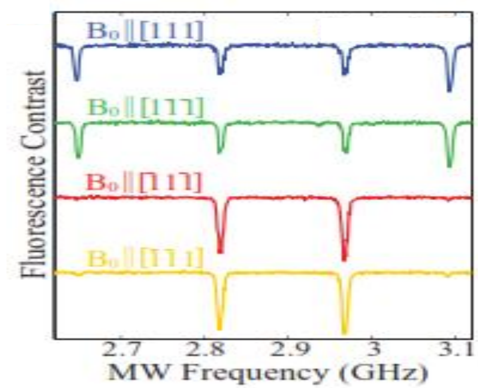
At **step edges of a (100)-grown** CVD diamond→ 50% preferential orientation

(100)





ODMR spectra



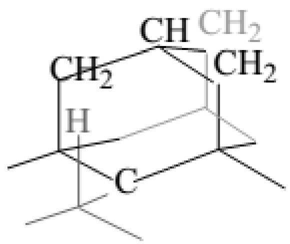
L. M. Pham et al., Phys. Rev. B 86 (2012) 121202

A. Edmonds et al., Phys. Rev. B 86 (2012) 035201

2. Controlling NVs orientation

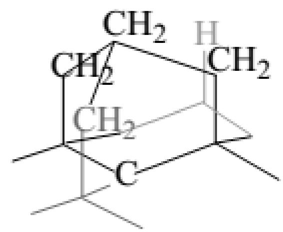
Growth on (111) orientation

Twinning is very likely to occur during the nucleation of next layer on <111>



Normal stacking

Small energy difference

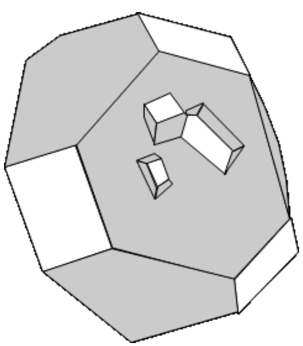


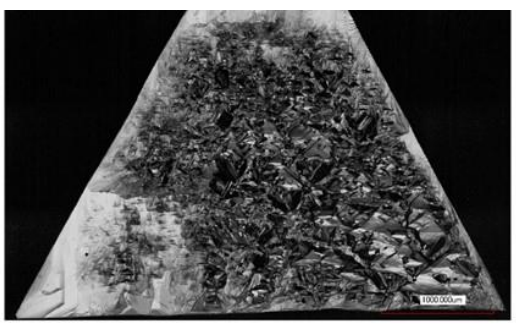
Twinned stacking

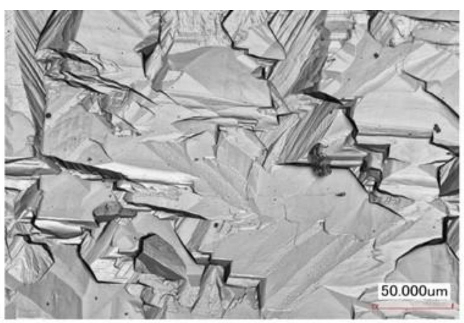
<111>

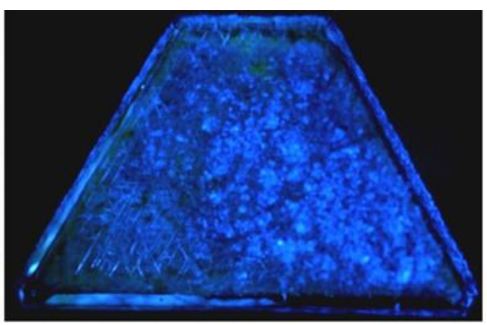
J.E. Butler et al. Philosophical Transactions of the Royal Society A 366 (2008) 295-311.

Under normal conditions, once a twin is formed it grows larger









(111) growth

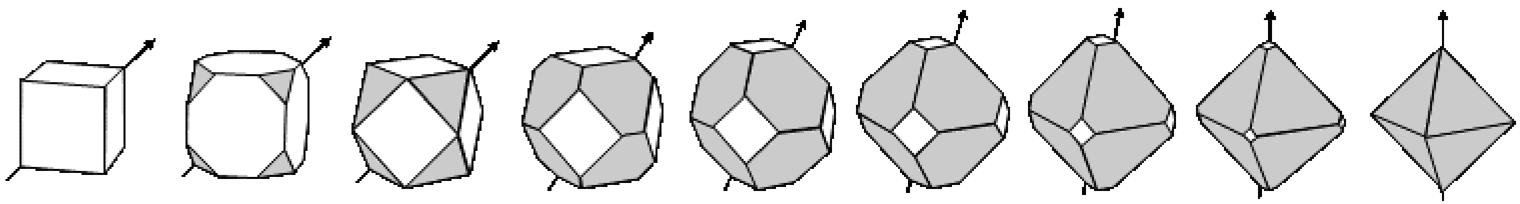
2. Controlling NVs orientation

Growth on (111) orientation

"A crystal facet is stable with respect to twinning, if an infinitesimally small twin attached to that facet disappears. It is unstable, if the twin grows larger."

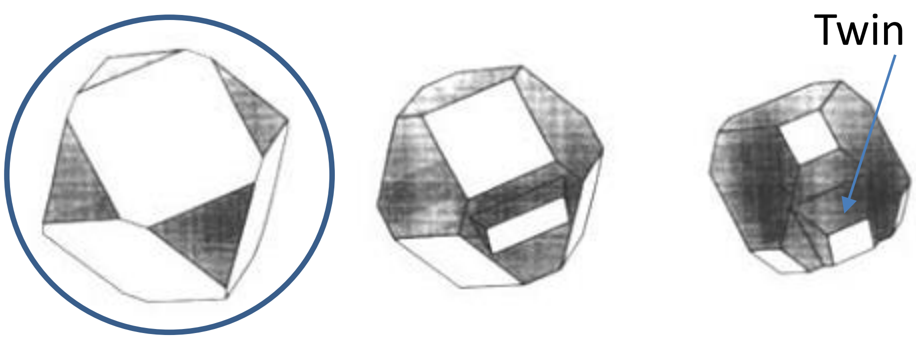
C. Wild et al. (1994). Diamond and Related Materials 3 373-381.

Alpha represents the relative growth rates of the (100) and (111) planes



$$\alpha = \sqrt{3}\,\frac{G_{100}}{G_{111}}$$

α =1.0 α =1.5 α =2.0 α =2.5 α =3.0



$1 < \alpha < 1.5 < \alpha < 2 < \alpha < 3$

For α < 1.5 the twin is overgrown by its parent facet…

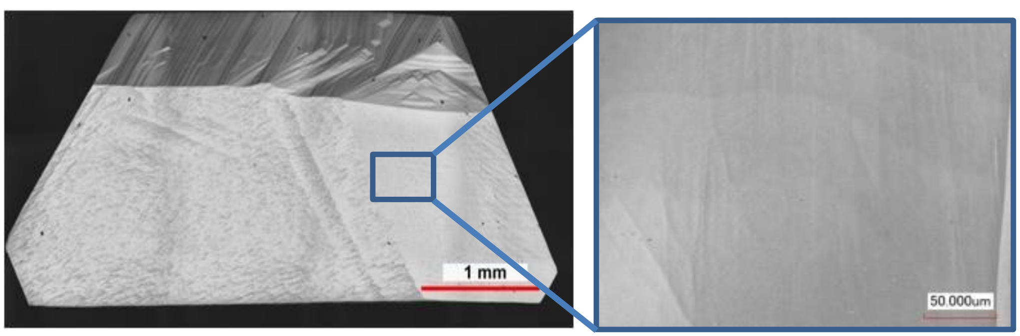
2. Controlling NVs orientation

Growth on (111) orientation

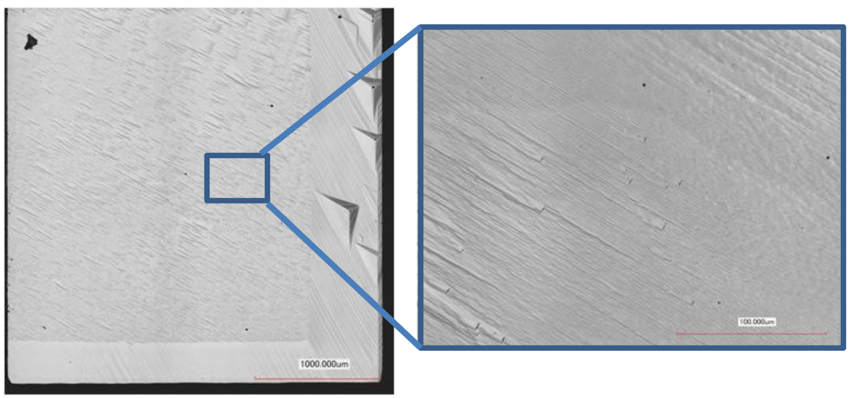
High growth temperature of **1050°C** and low methane concentration of **2%**
High power densities: **250 mbar and 3.5 kW**

→ No measurable growth on (100) → 6µm/h on (111) → **α << 1.5**

On HPHT substrates from Sobolev Institute



On CVD substrates from Element 6



Smooth surface for up to 200 µm-thick films

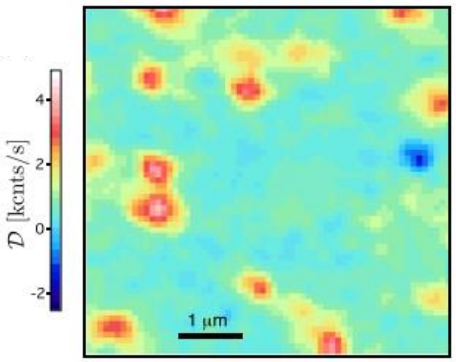
A. Tallaire et al. (2014).Diamond and Related Materials 41 34-40.

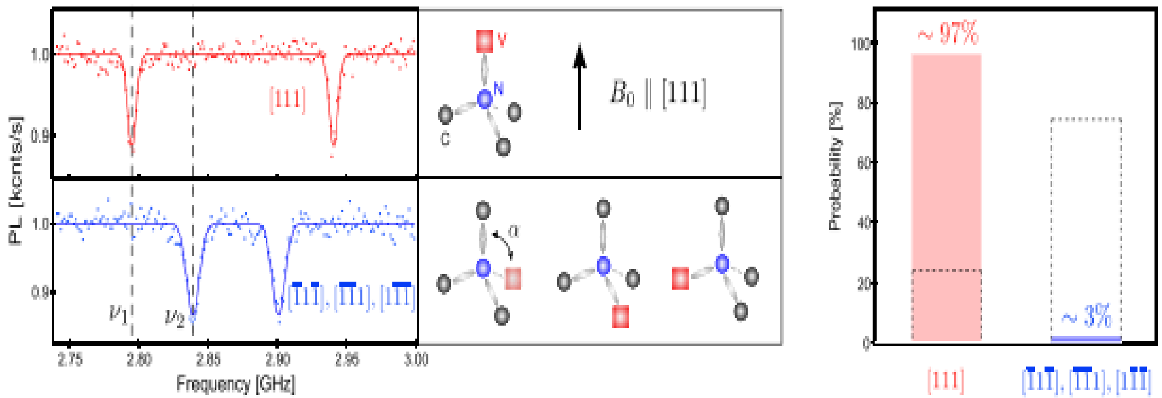
2. Controlling NVs orientation

Growth on (111) orientation

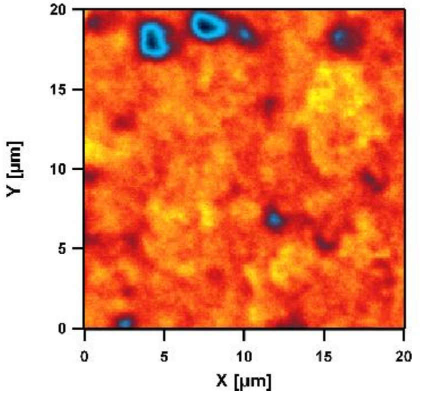
Almost 100 % orientation of NV defects!

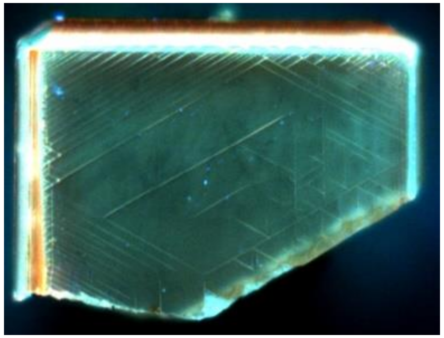
M. Lesik et al., APL 104, 113107 (2014)





Heavy doping difficult





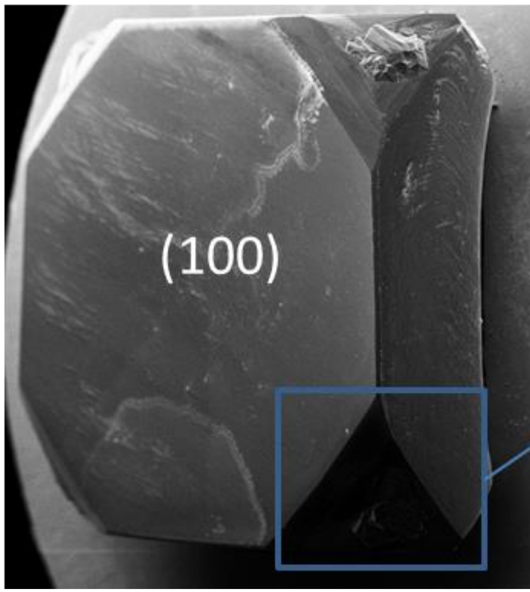
Cracking, non uniformity, loss of preferential orientation

Collab. ENS Cachan/LAC-CNRS and Thales

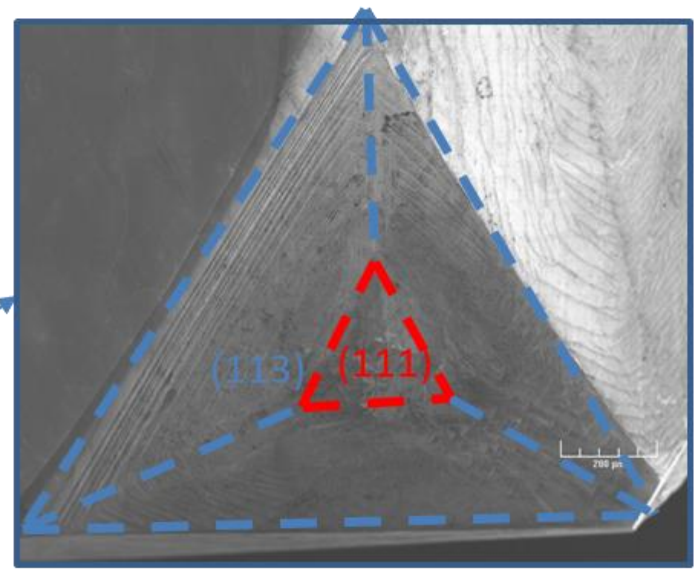
2. Controlling NVs orientation

Growth on (113) orientation

Standard growth on (100)



3 {113} facets formed at the corner

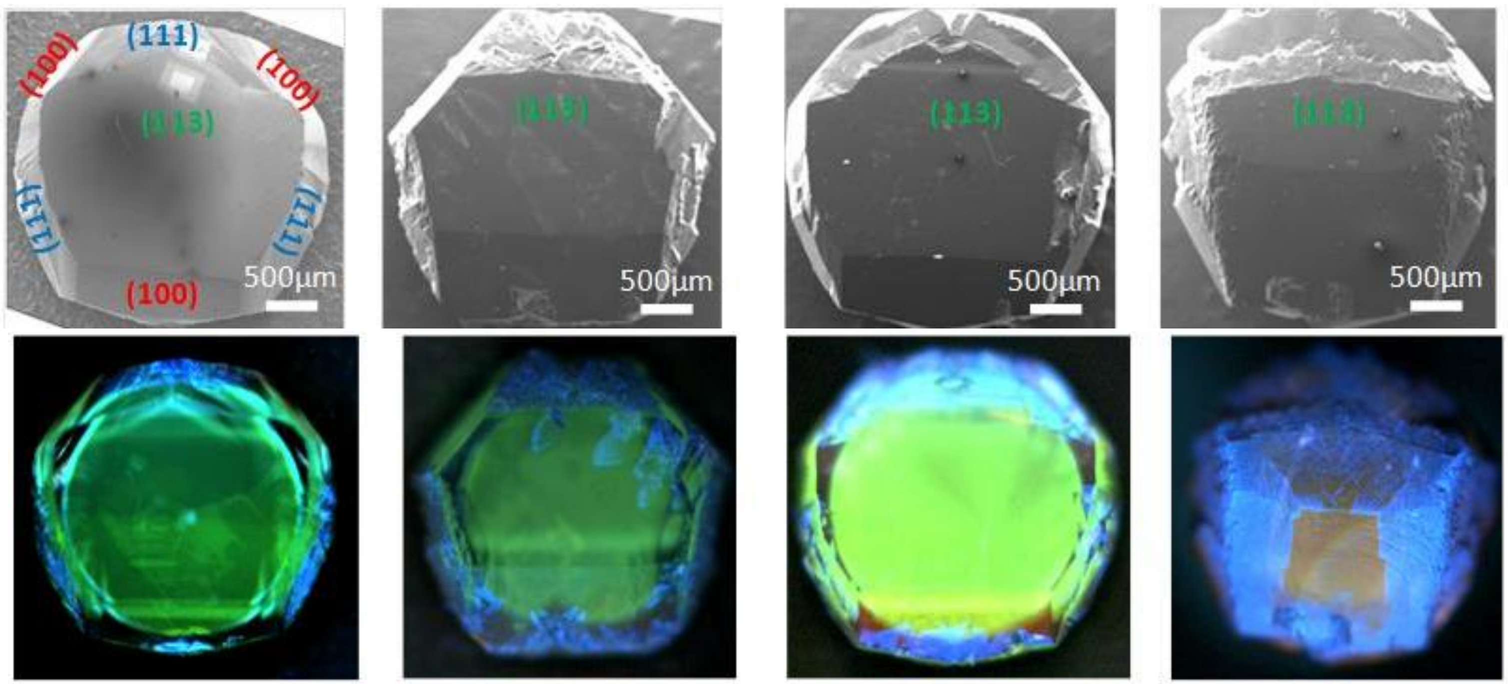


2. Controlling NVs orientation

Growth on (113) orientation

Growth carried out under standard conditions: High plasma power densities (220-250 mbar 3-3.5kW) ; 800°C<T<1000°C ; 4% CH_4

0 ppm N_2	0.5 ppm N_2	10 ppm N_2	50 ppm N_2

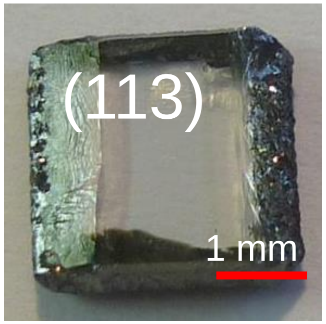


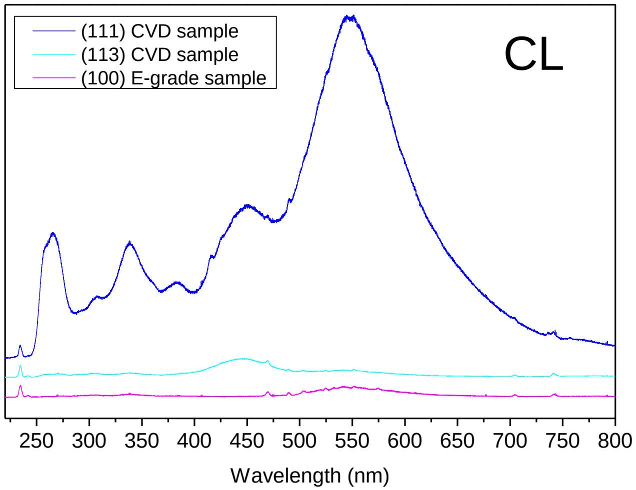
460 µm	760 µm	500 µm	1450 µm
15 µm/h			50 µm/h

M. Lesik et al. (2015) Diamond and Related Materials 56 (2014) 47

2. Controlling NVs orientation

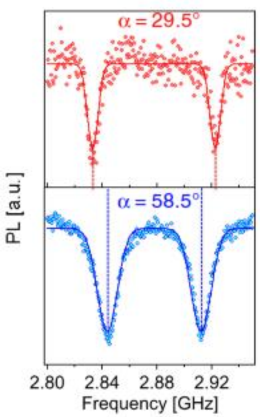
Growth on (113) orientation

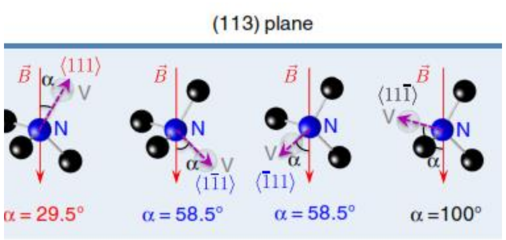


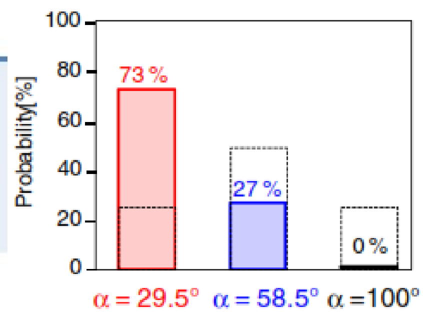


Thick films at high growth rates
Higher crystalline quality than (111)
No stress

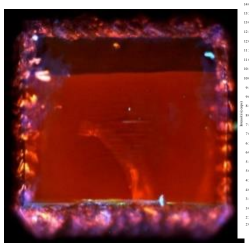
73% preferential orientation

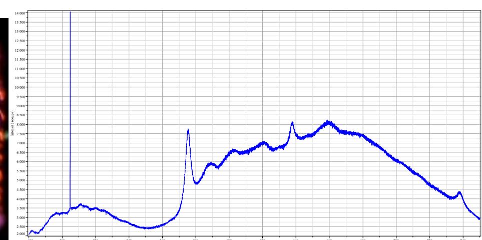






High doping possible





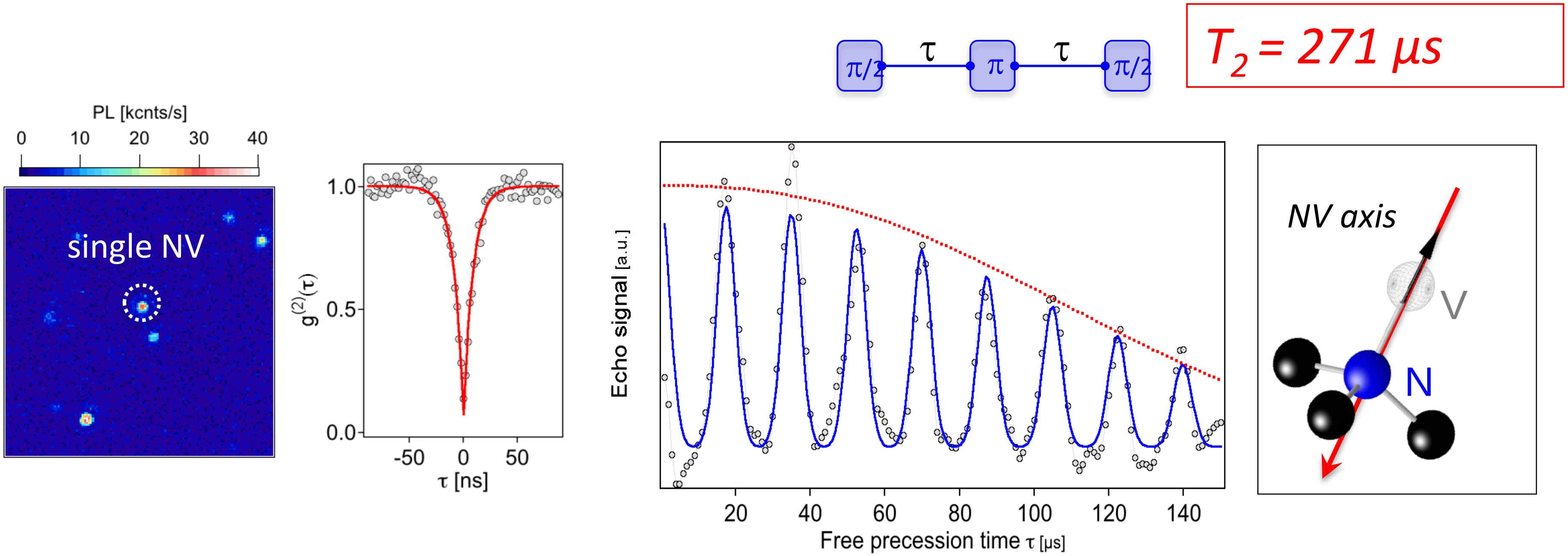
50 ppb NV⁻

M. Lesik et al., Diam. & Relat. Mat. 56, 47-53 (2015).

Collab. ENS Cachan/LAC-CNRS and Basel University

2. Controlling NVs orientation

Growth on (113) orientation



Single NVs exhibit coherence time comparable to that obtained for high quality CVD films with similar isotopic purity on standard (100)

Despite only partial preferential orientation: (113) is an interesting platform for NV centers

M. Lesik et al. (2015) Diamond and Related Materials 56 (2014) 47

2. Controlling NVs orientation

	Conventional (100)	(111)	(113)
Substrates availability	++	+	-
Range of growth conditions	+	-	++
Growth rates	+	+	++ (x2)
Crystalline quality	++	-	++
NV center orientation	- (25%)	++ (100%)	+ (73%)
N doping efficiency	-	++	+

3. Controlling NVs spatial localization by direct CVD growth

i. Controlling NVs in depth

Create spatially localized NVs by direct CVD growth

Ultra-pure, high quality CVD diamond preferably ^{12}C enriched

Thin layer containing a lot of NVs close to the surface

IDEAL STRUCTURE

Challenge : grow thin highly doped layers

1. Control thickness

$$Th = GR \times t$$

Reduce growth rate?

2. Control interface sharpness

$$t_{resid} = \frac{V_{chamber} \times P}{F_{total} \times P_{ATM}}$$

Reduce residence time?

3. Control NV density

$$N_{NV} = yield \times \eta_{incorp.} \times [N_2]$$

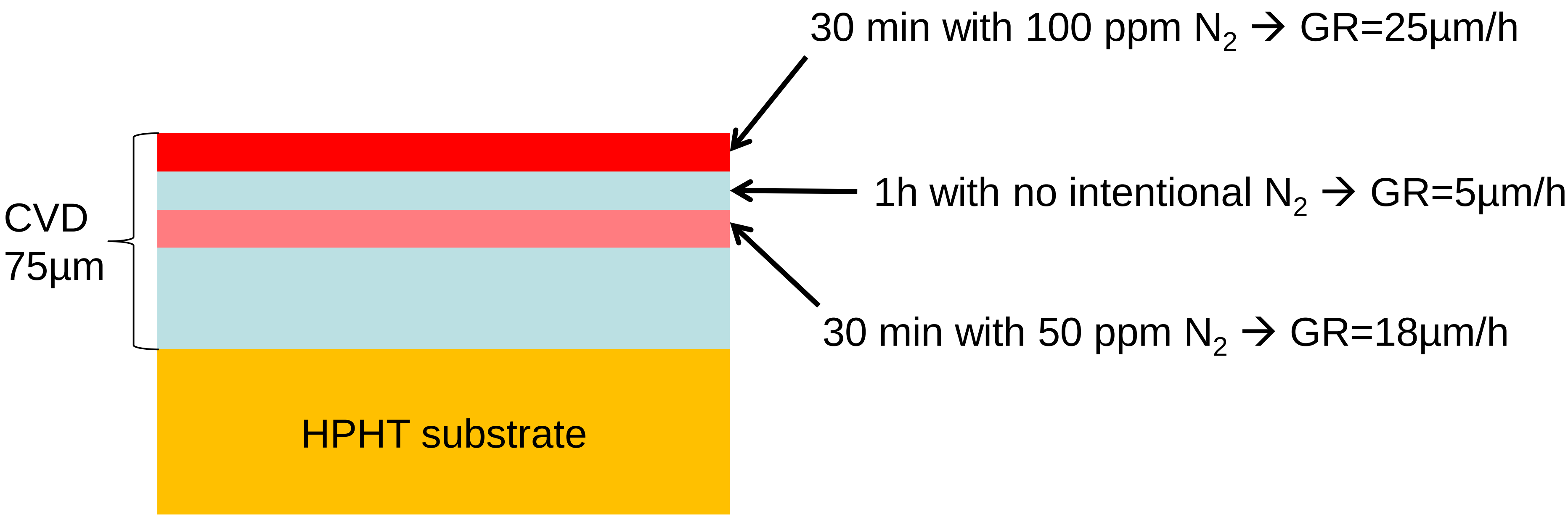
Improve incorporation efficiency?

i. Controlling NVs in depth

1. Changing gas phase composition

Keep growth conditions the same --- Vary the gas phase composition

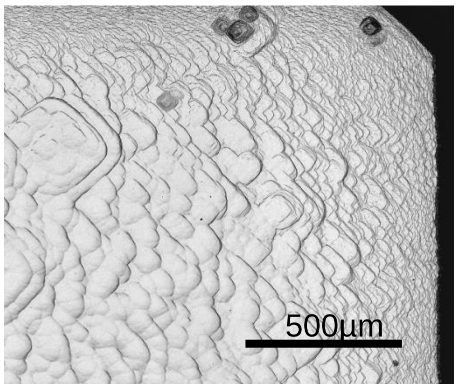
Chamber volume = 20L Residence time = 15min @ 500sccm



i. Controlling NVs in depth

1. Changing gas phase composition

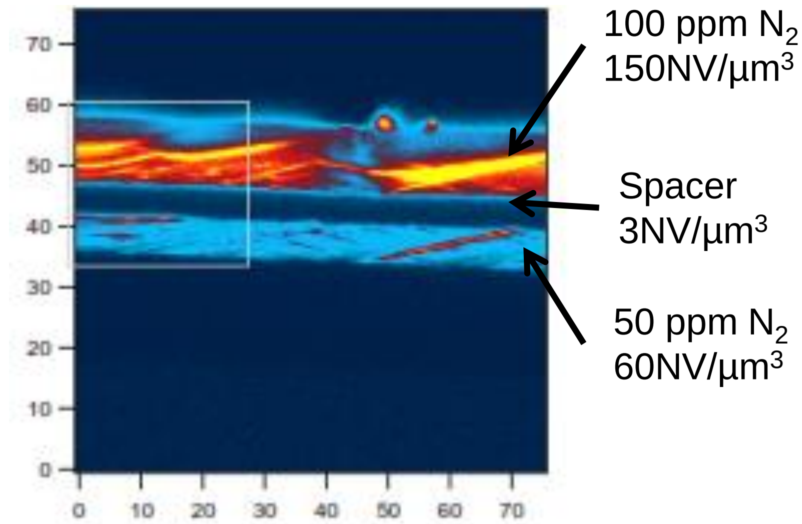
Laser microscope image of the surface

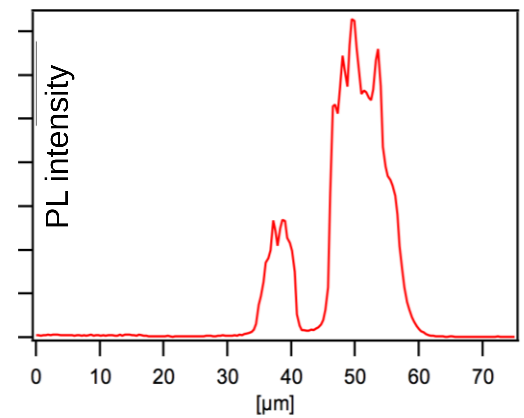


Good morphology despite presence of step bunching due to nitrogen

Tallaire DRM15 1700 2006

Confocal scan of the cross-section





Possible to control NV density with N_2

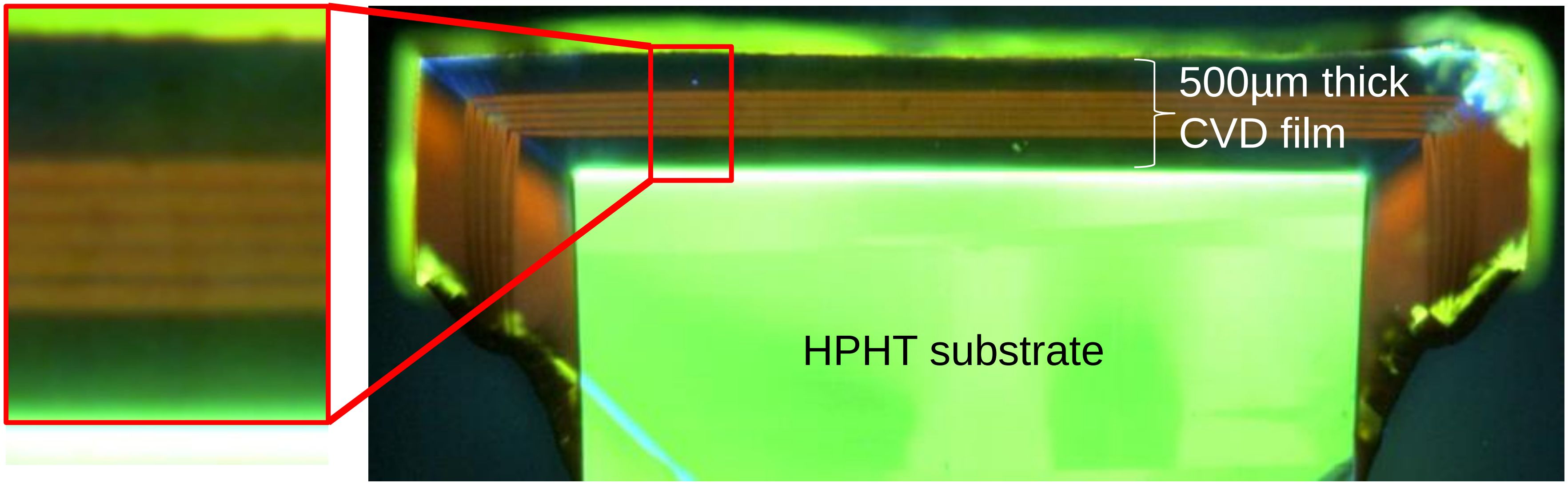
Good contrast between N-doped and N-free regions

i. Controlling NVs in depth

1. Changing gas phase composition

Same experiment with 5 stacked layers

1h with no intentional N_2 → GR = 7µm/h
1h with 50 ppm N_2 → GR = 30µm/h
X5



Cross section luminescence image

Possible to stack layers of different doping while keeping good crystalline quality

→ Difficult to obtain thin layers with sharp interfaces using this technique

i. Controlling NVs in depth

2. Changing growth temperature

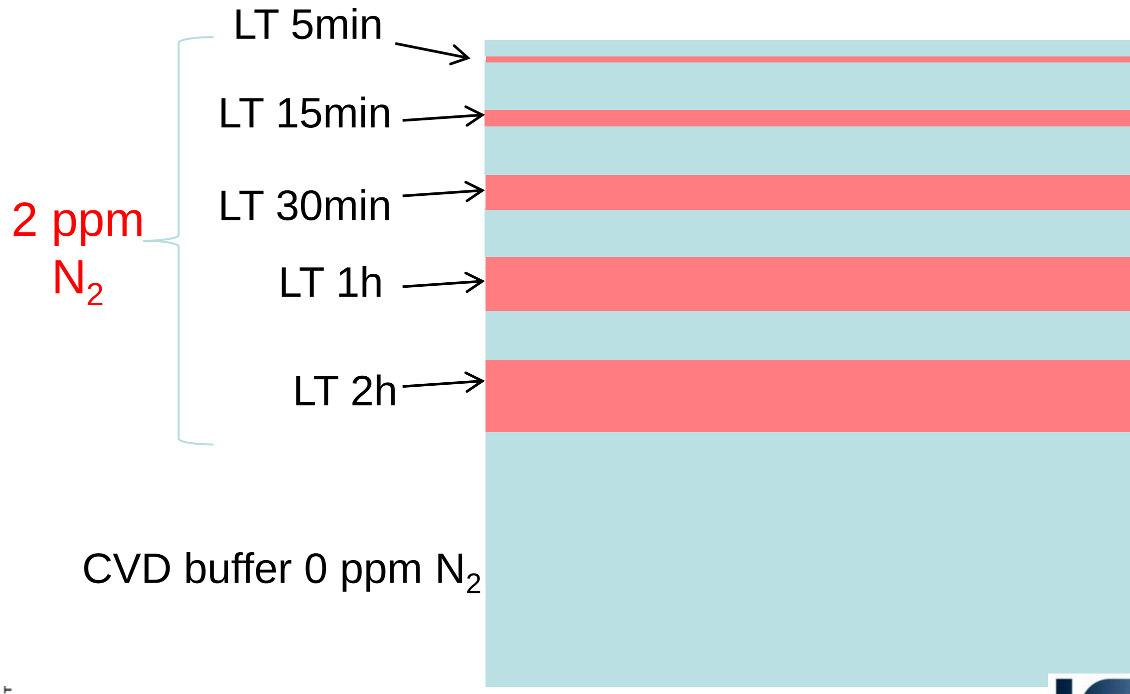
Keep the gas phase composition the same --- Vary growth temperature

Nitrogen incorporation strongly temperature dependent
Temperature changed abruptly by a slight decrease of pressure/power

Low T layer @ 760°C and reduced growth time

separated by

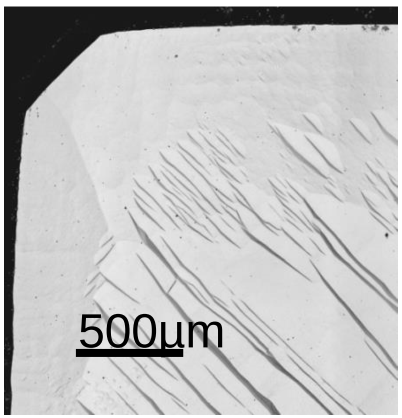
High T spacer 45min @ 840°C



i. Controlling NVs in depth

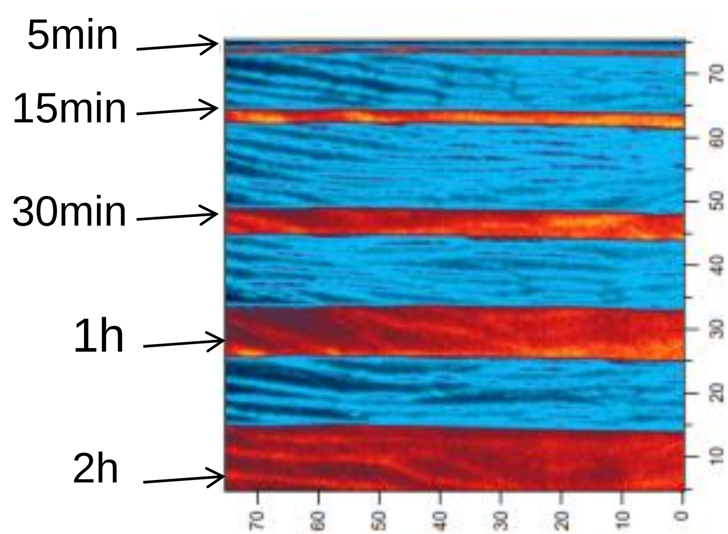
2. Changing growth temperature

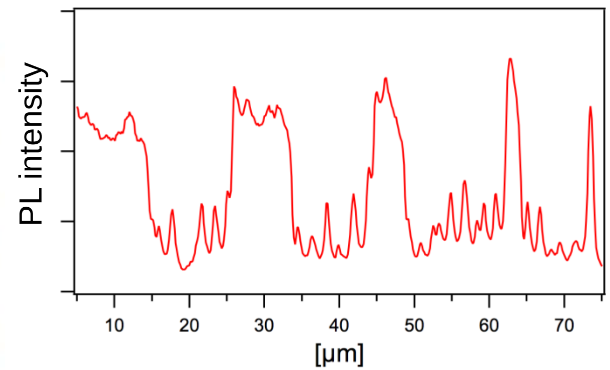
Laser microscope image of the surface



Lower step bunching due lower N_2 addition (2 ppm)
Good morphology

Confocal scan of the cross-section





LT layer 220-285 NV/µm^3 HT layer 50-140 NV/µm^3

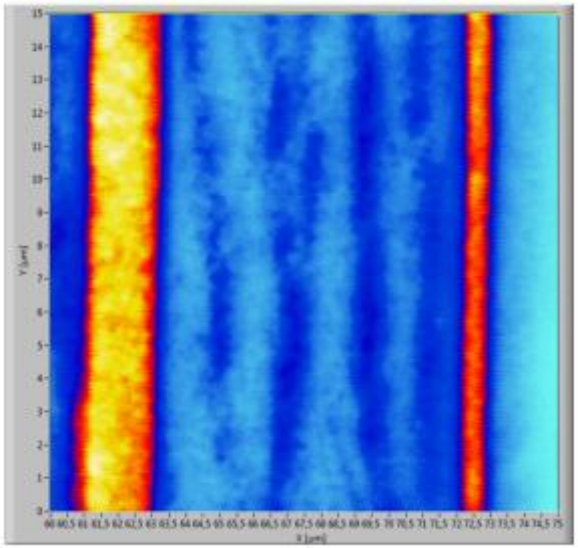
Larger amounts of NVs at low temperature (X2 to X5 contrast)

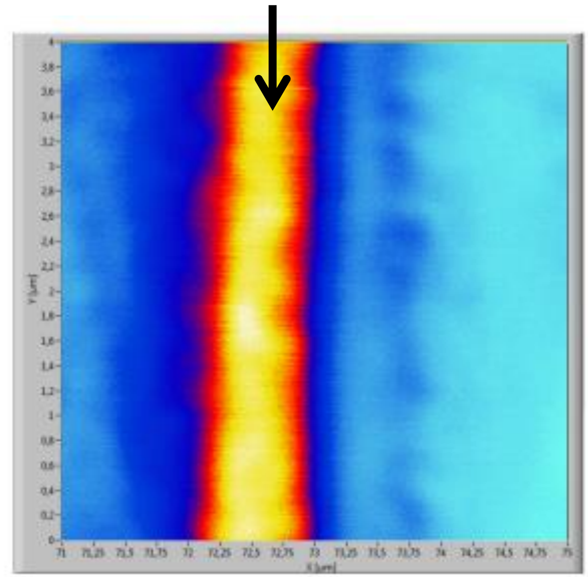
Reduce thickness by reducing growth time

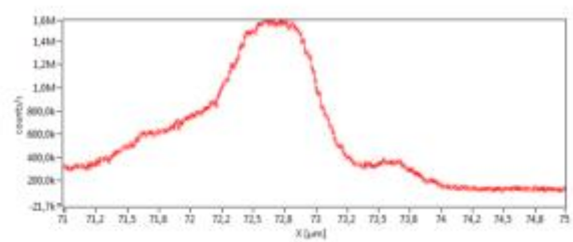
i. Controlling NVs in depth

2. Changing growth temperature

The thinnest line

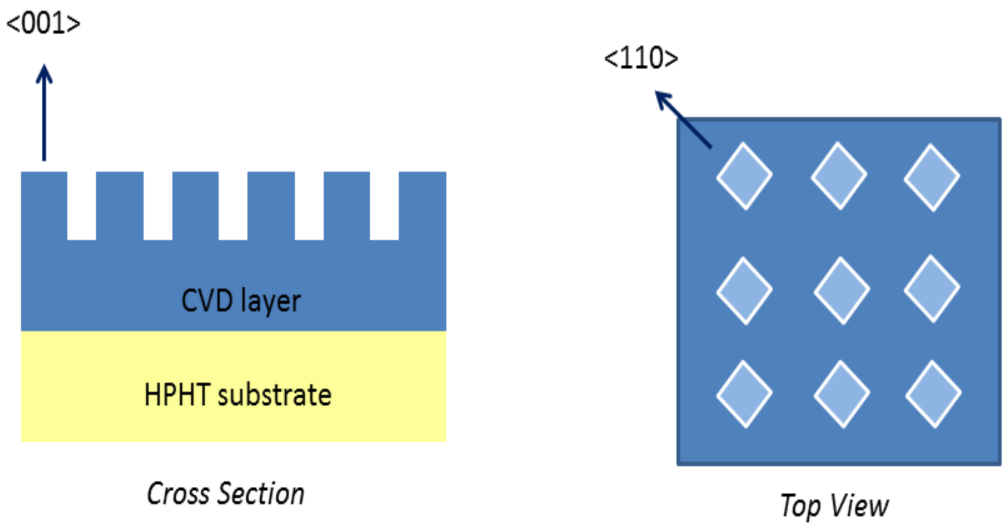






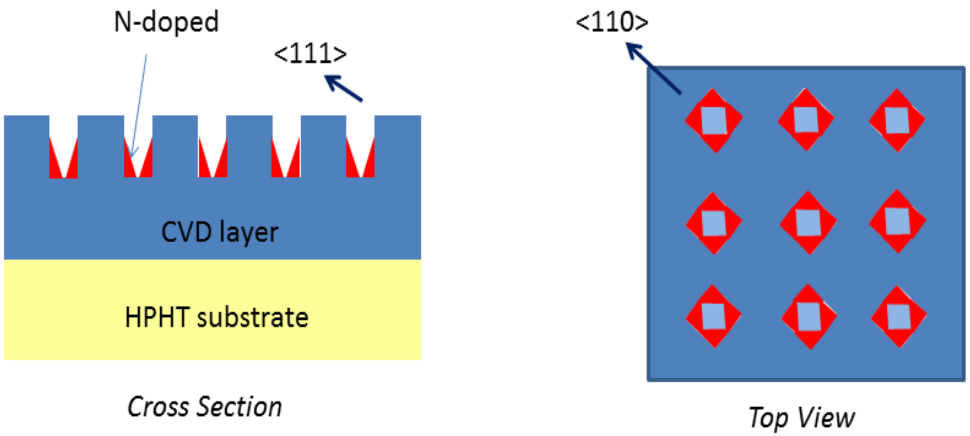
Thickness down to about 300 nm (perhaps diffraction limited)

ii. Controlling NVs at the surface



Step 1

Structuration of pits array in single crystal diamond by microfabrication



Step 2

Selective growth under very low alpha value with added nitrogen

ii. Controlling NVs at the surface

Step 1

Structuration of pits array in single crystal diamond by microfabrication

(1) Silicon dioxyde deposition by PECVD

(2) UV insolation of photoresist

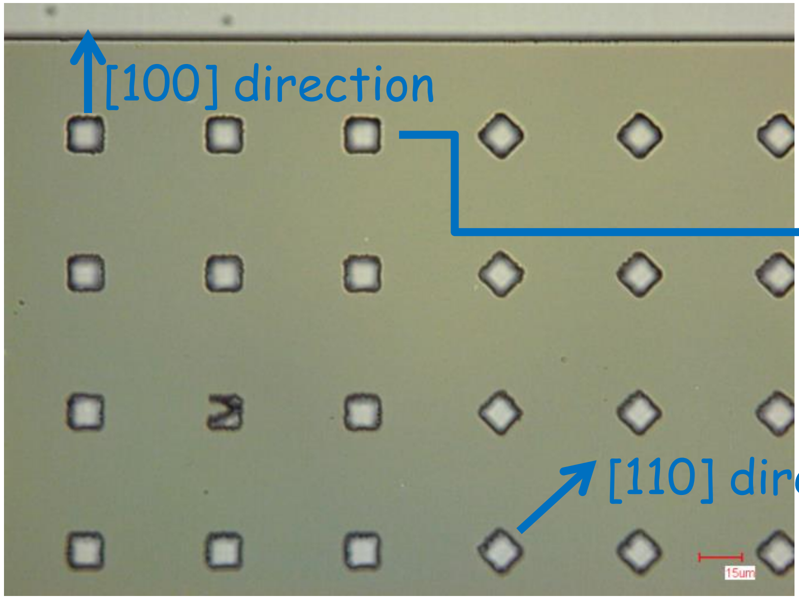
(3) SiO_2 ICP etching (fluorine discharge)

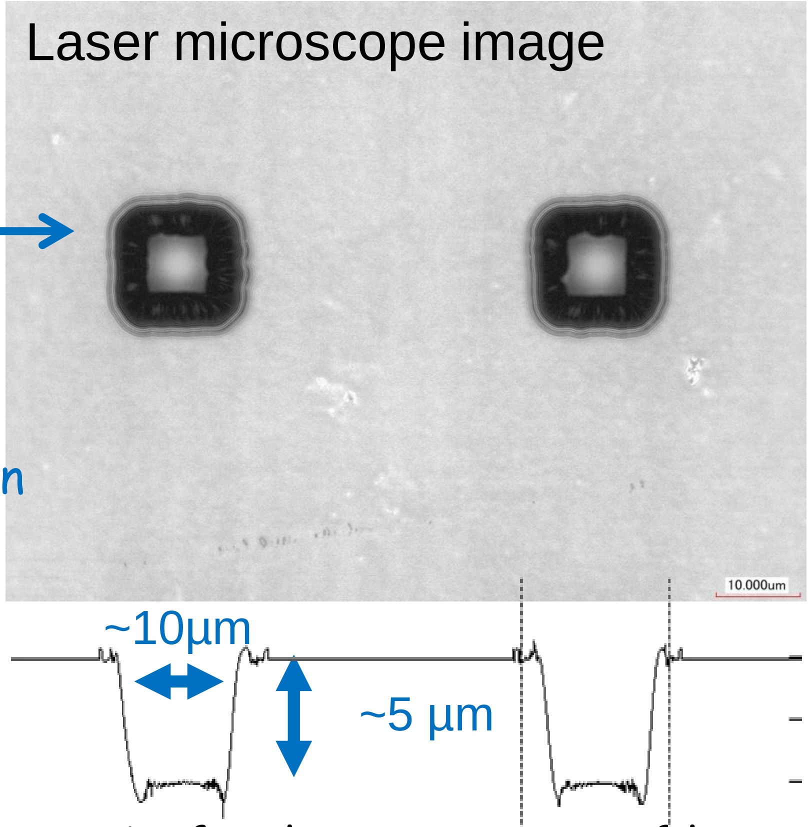
(4) Diamond ICP etching (oxygen discharge)

ii. Controlling NVs at the surface

Step 1

Observation of pits array on the diamond surface





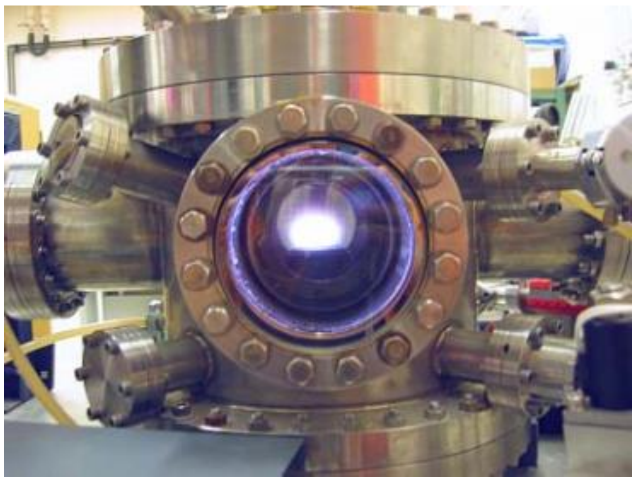
(100) and (110) oriented pit array

Confocal microscope profil

ii. Controlling NVs at the surface

Step 2

Create in-situ NV center during PACVD diamond growth



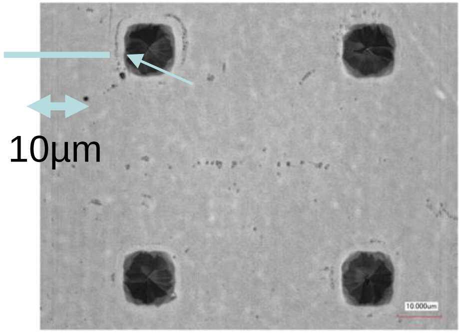
T= 1050°C
1% CH_4
200mbar, 3kW
1ppm N_2

- Addition of nitrogen during growth
- Choice of conditions for which growth is promoted in the <111> directions

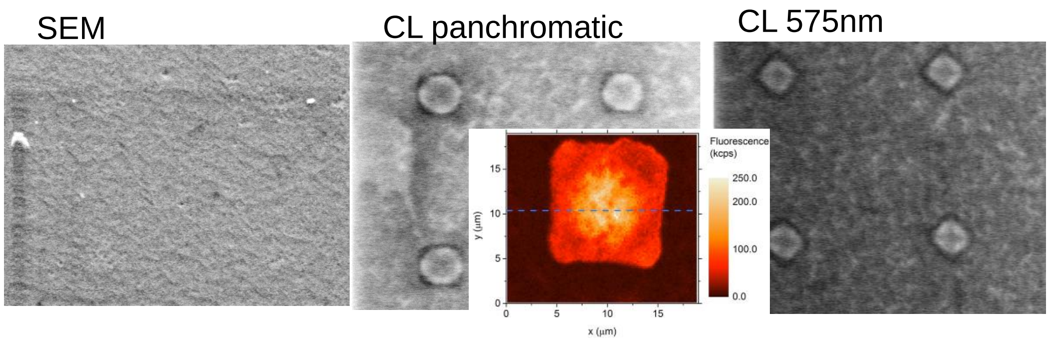
A. Tallaire et al., DRM 41 (2014) p34

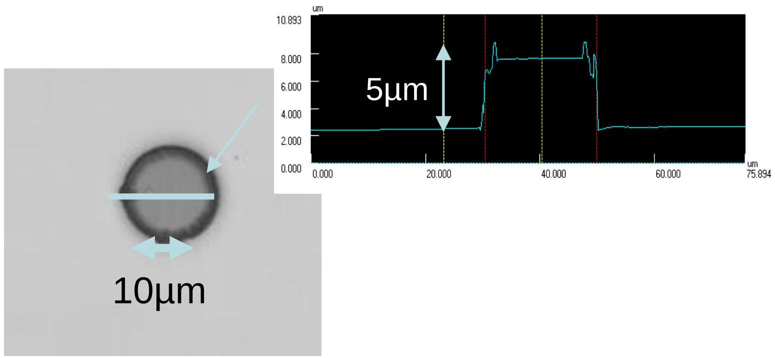
ii. Controlling NVs at the surface

Etching pattern → Local growth → PL/CL analysis

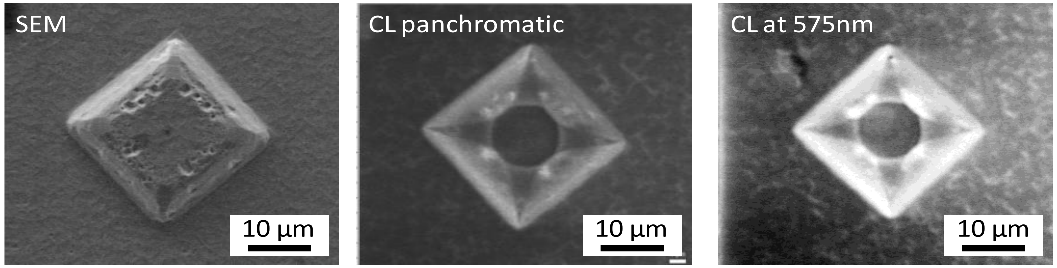


Overgrowth on holes



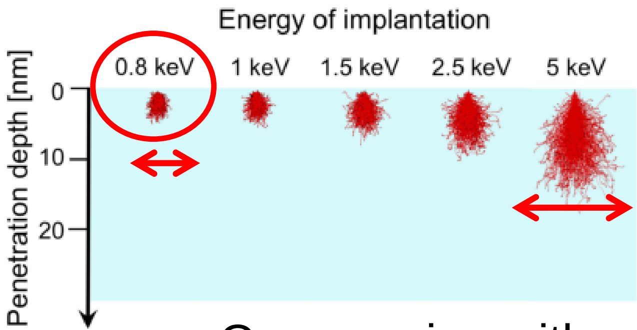


Overgrowth on micro-pilars



Possibility to create spatially localized NV centres by direct CVD growth

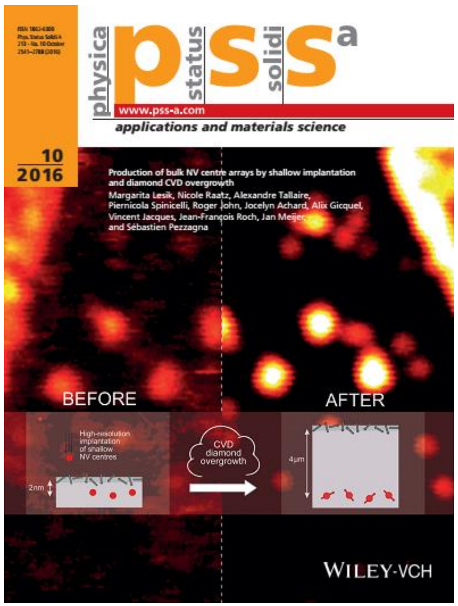
iii. Bringing NVs close to the surface

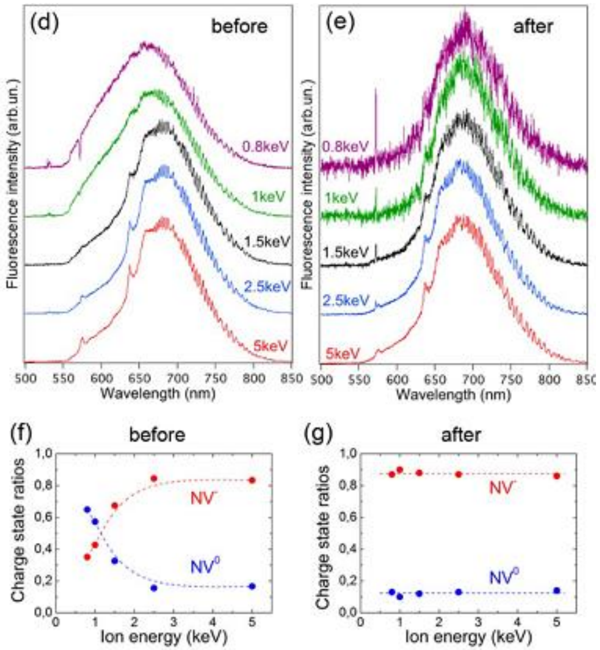


Low energy implantation → accurate positionning but low yield and sensitive to surface defects

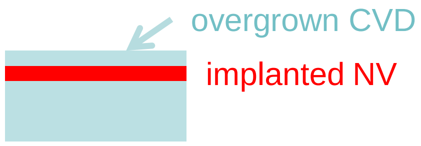
Overgrowing with a thin CVD layer → improvement of NV properties

Staudacher et al. APL101, 212401-212404 (2012).





Need to find the right overgrowth conditions → preserve etching pattern while keeping high quality/purity



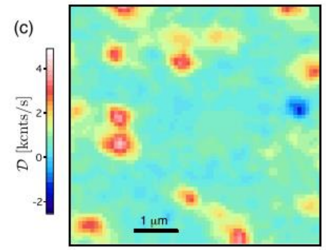
Stabilize NV^- charge state

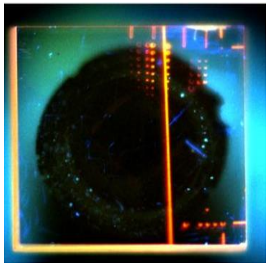
M. Lesik et al. physica status solidi (a), 213 (2016) 2788-2788.

CONCLUSIONS

NV centres in diamond : a robust qubit system

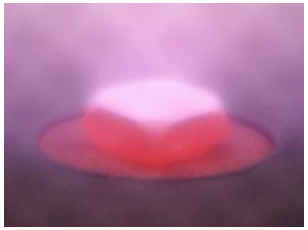
- High magnetic sensitivity
- Nanoscale sensors @RT
- Bright single photon source

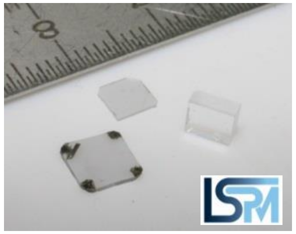




PACVD technique : a key enabling technology

- Unrivalled purity (isotopic control)
- High flexibility (multilayer, thin/thick films)
- In situ doping of NVs and other defects…





Challenges lying ahead

- Growing layers with heavy NV doping (1ppm?) and preferential orientation
- Thin « delta-doped » layers by CVD or well controlled patterns
- Find alternative defects to NVs (SiV and others…)
- Integrate diamond into other platforms

Special thanks to colleagues and collaborators:

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Leipzig University:
S. Pezzagna, J. Meijer

http://www.diadems.eu

Quantera Microsens

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Thank you for your attention