Molecular and carbon-based electronic systems

Diamond films and particles

- Diamond structure
- Optical and thermal properties
- Diamond synthesis
- Defects
- Nanodiamonds
- Detection of NV-centers

Input & slides from Patrick Maletinsky & Stepan Sthelik!

University of Basel

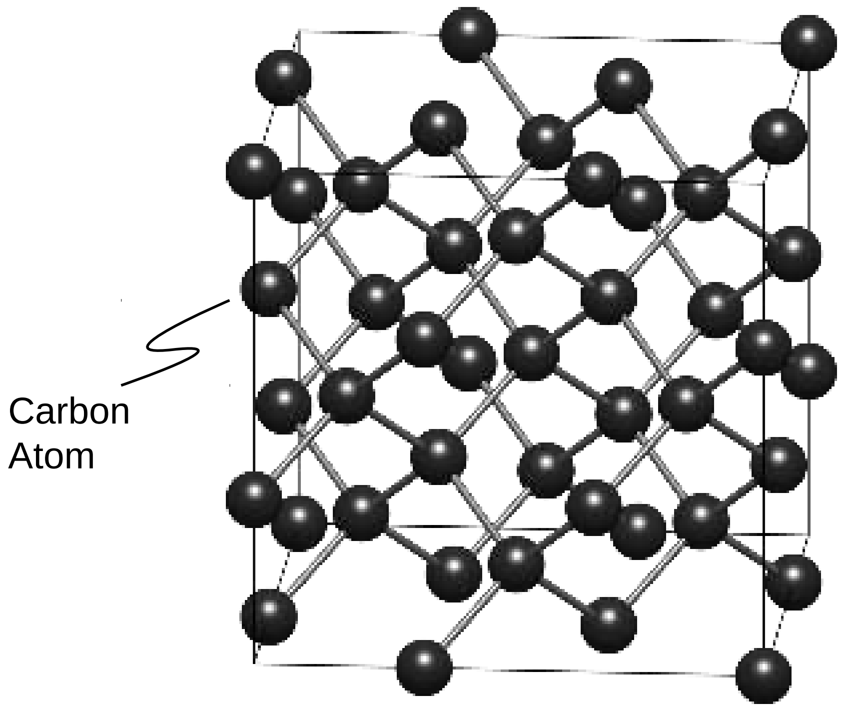
Department of Physics

Thilo Glatzel, thilo.glatzel@unibas.ch

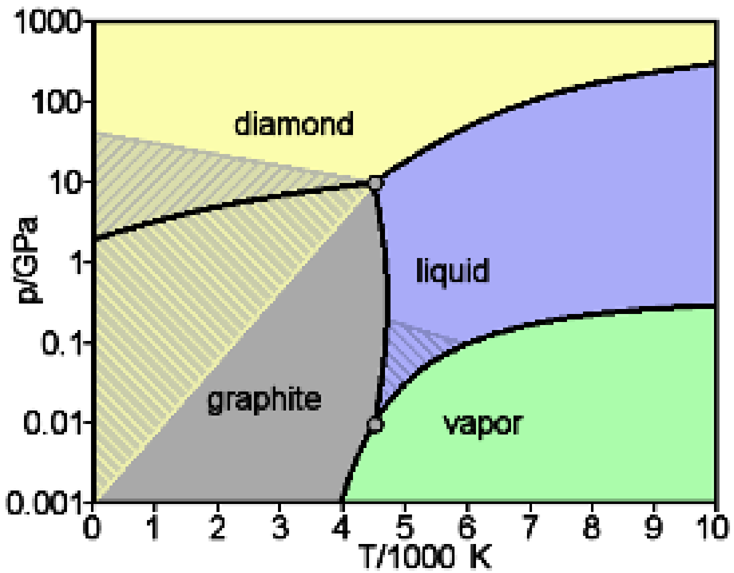
SWISS NANOSCIENCE INSTITUTE

Structure of Diamond

carbon atoms are arranged in a variation of the face-centered cubic crystal structure called "*diamond lattice*"

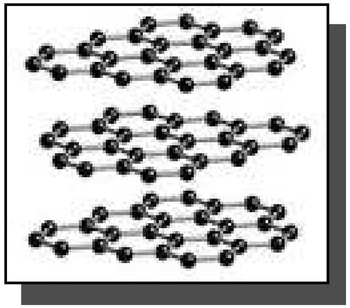


Theoretically predicted phase diagram of carbon



triple point at 10.8 ± 0.2 MPa
and 4600 ± 300 K

Similar to coal, HOPG, or graphene



General properties of diamond

The most important properties of diamond are the

- unsurpassed hardness
- extremely high thermal conductivity
  (>1800 W/mK, five times that of copper)
- broad band optical transparency
- extremely chemically inert:
  Not affected by any acid or other chemicals
- Graphitization only at very high temperatures
  (T > 700°C in an oxygen containing and 1500°C in an inert atmosphere

Properties of diamond

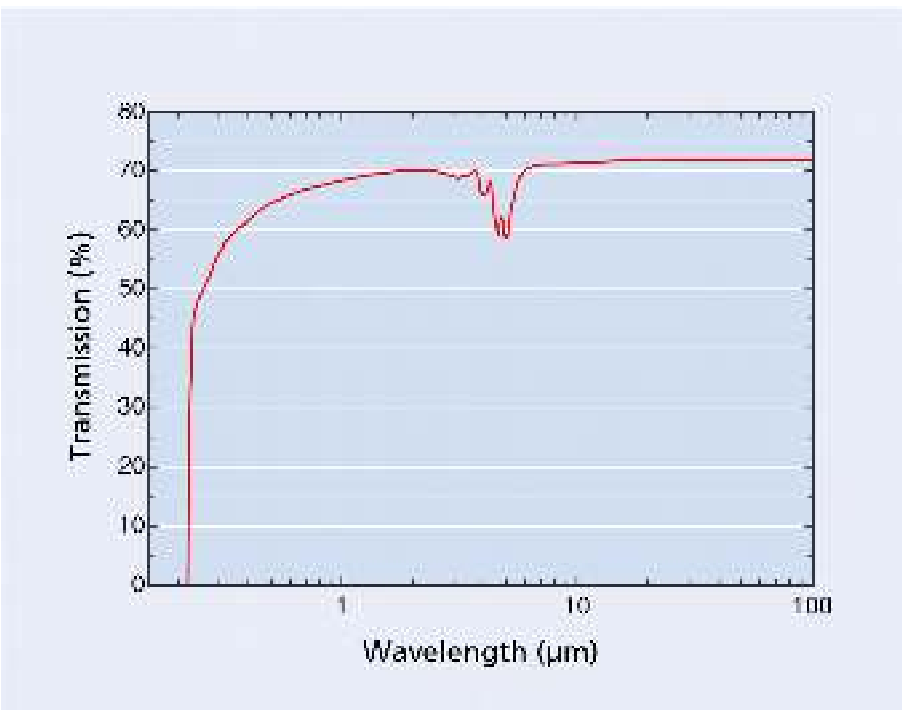
Property	Value
Vickers hardness*	10,000 kg/mm^2
Young's modulus*	1050 GPa
Poisson's ratio	0.1
Density	3.515 g/cm^3
Atom density*	1.77×10^{23} $1/cm^3$
Thermal expansion coefficient	1.0×10^{-6}/K @300K
Sound velocity*	17,500 m/s
Friction coefficient	0.1
Specific heat @ 20°C	0.502 J/gK
Debye temperature*	1860±10K
Bandgap	5.45 eV
Resistivity	10^{13} - 10^{16} Ωcm

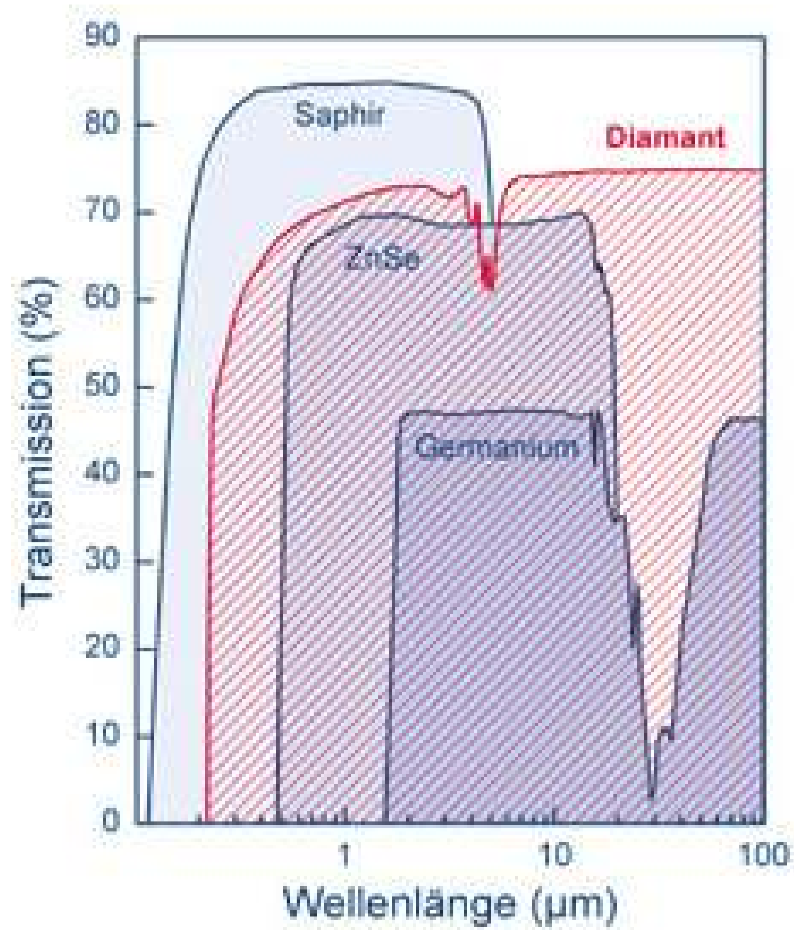
*highest value of all solid materials

http://www.diamond-materials.com

Optical Properties

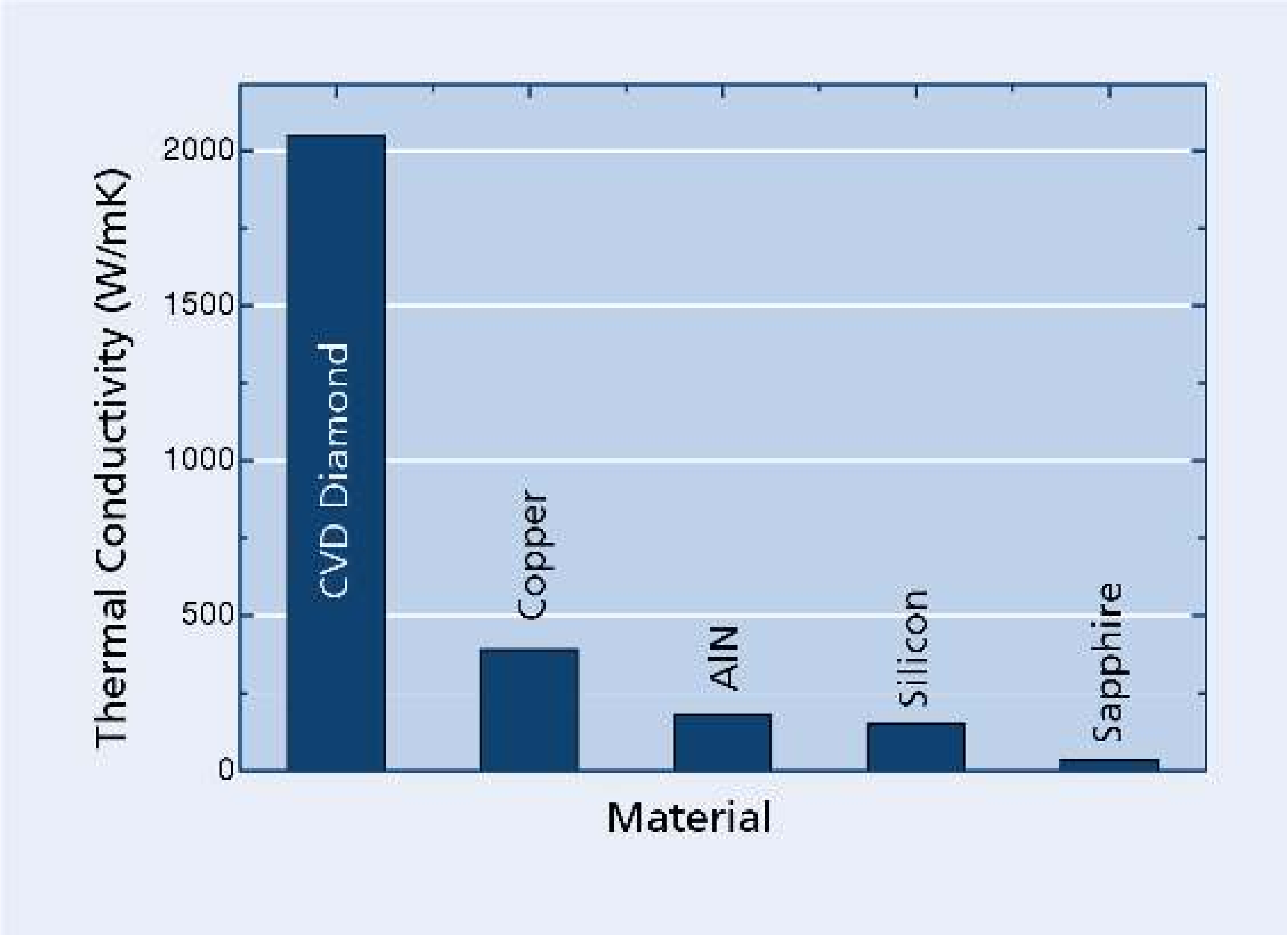
Property	Value
Transmission	225nm to far IR , > 70% @ 10µm
Refractive index	2.38 @ 10µm, 2.41 @ 500nm
Absorption coefficient	$< 0.10\ cm^{-1}$ @ 10µm
Bandgap	5.45 eV
Tensile strength (0.5mm thick)	
Nucleation surface in tension	600 MPa
Growth surface in tension	400 MPa
Loss tangent (tanδ @140 GHz)	< 2.0×10[illegible]
Dielectric constant	5.7



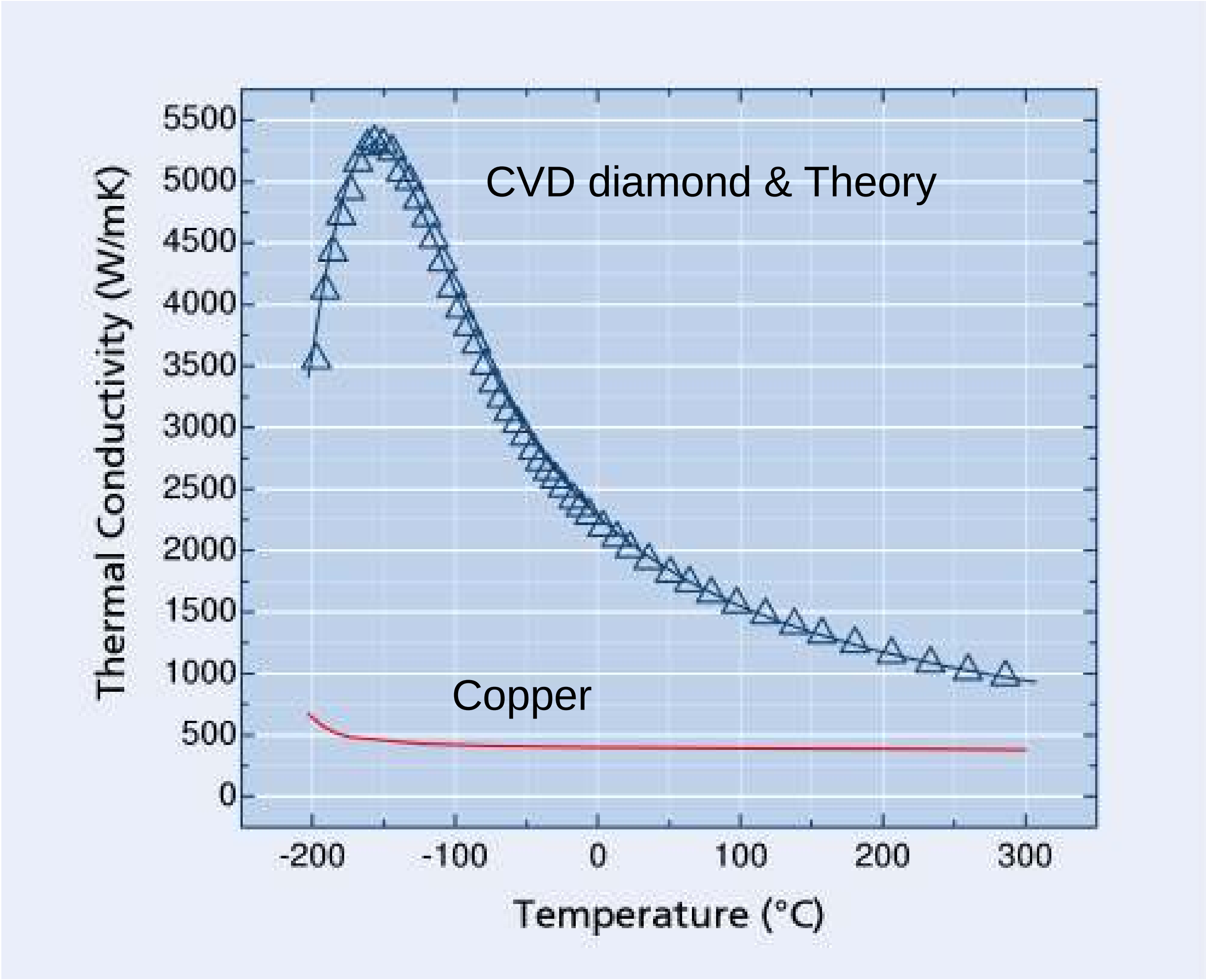


http://www.diamond-materials.com

Thermal Properties

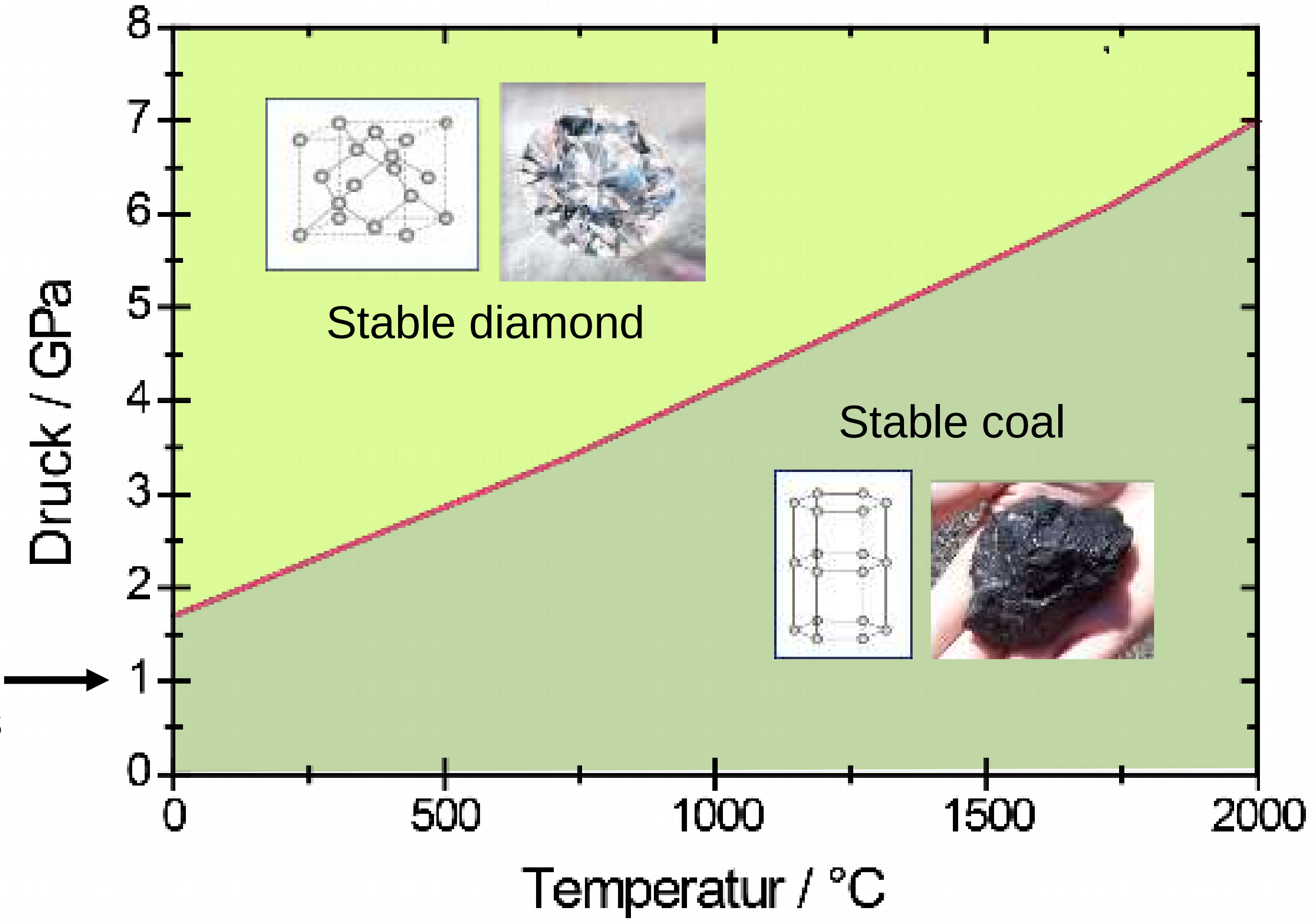


Thermal Properties



Phase diagram of carbon

10’000
atmospheres

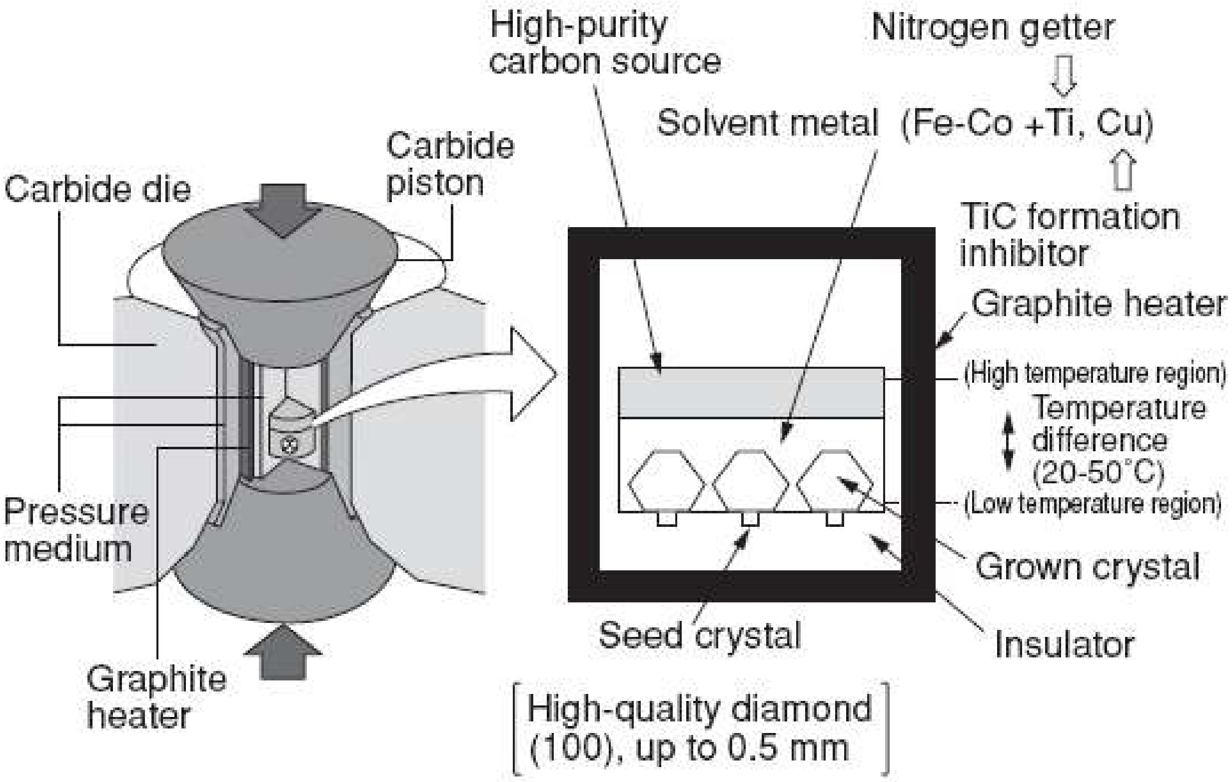


Synthetic Diamonds
high pressure and high temperature (HPHT)

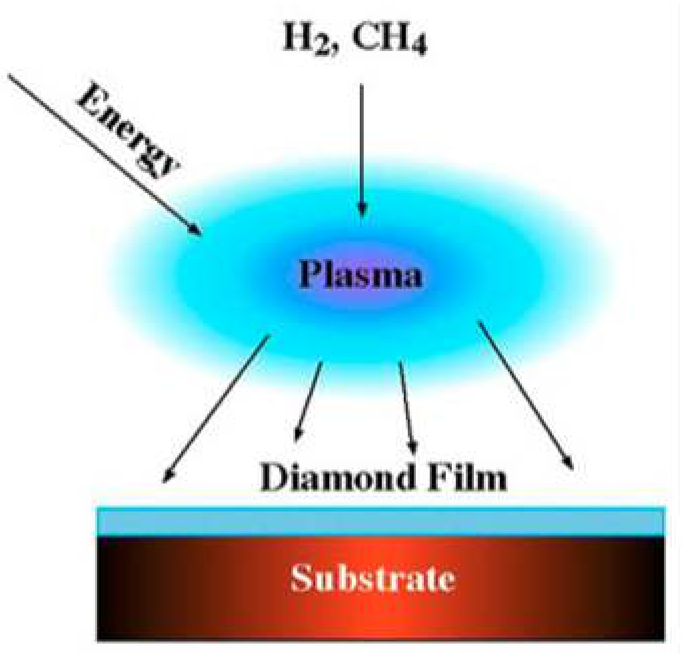
Yearly Production~4400Mio ct. = ~1000t

“natural” growth conditions at high temperatures and pressures (~6GPa & ~1500°C)

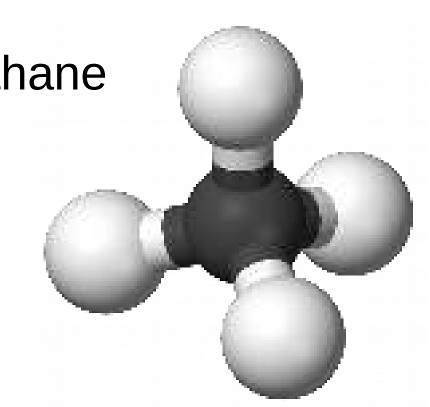
Synthetic Diamonds
high pressure and high temperature (HPHT)

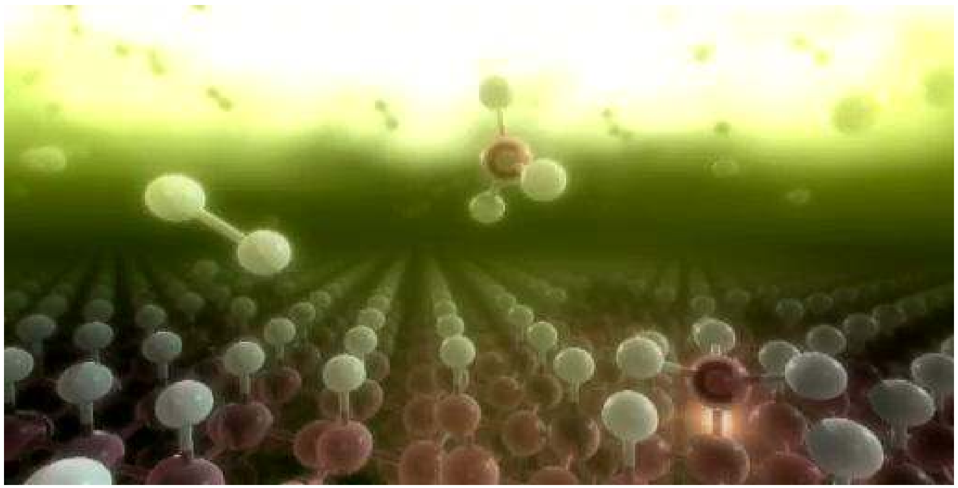


CVD Synthetic Diamonds



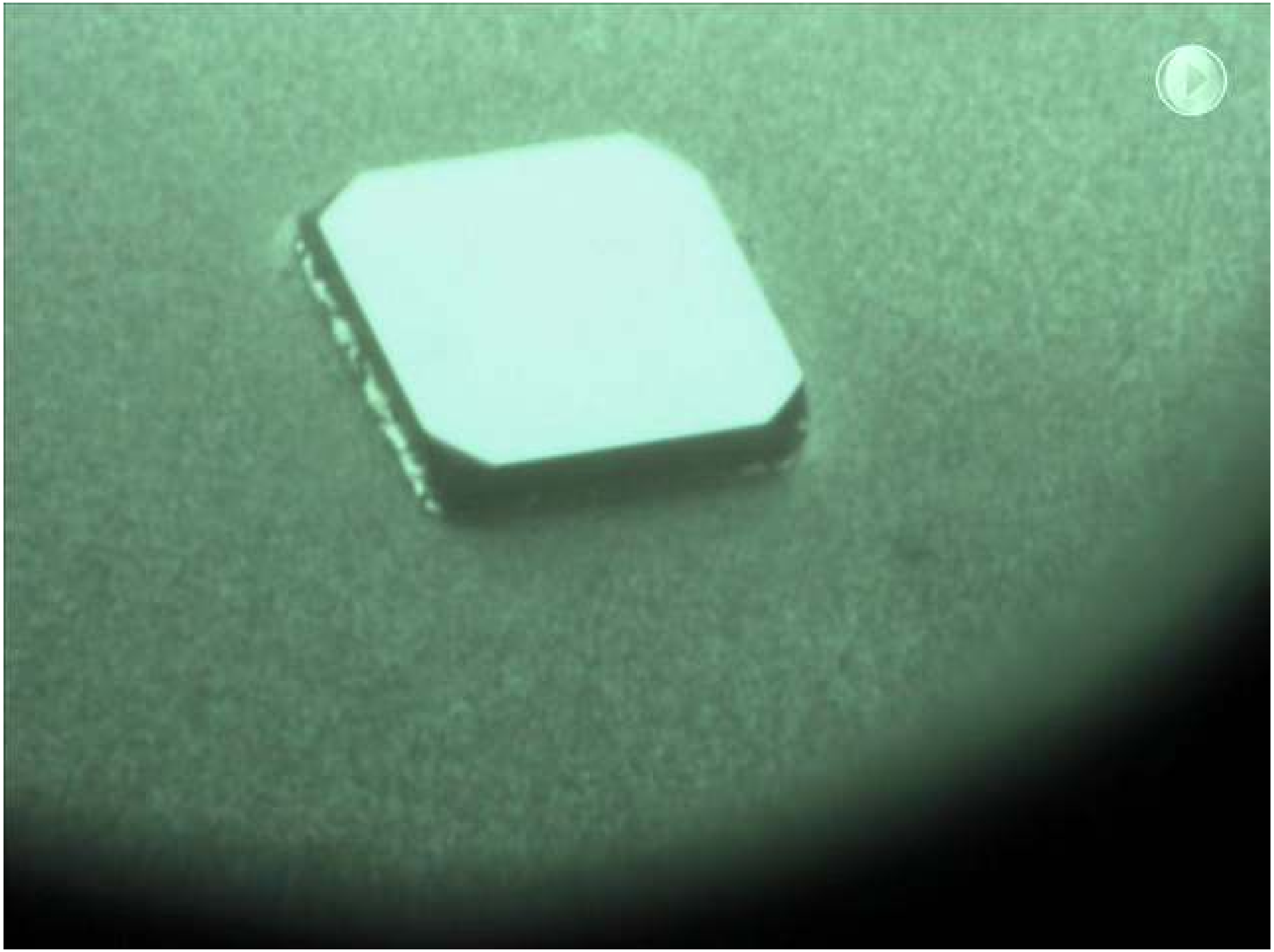
methane





low pressure and temperature growth
(~0.5GPa & ~700-1000°C)

CVD Synthetic Diamonds



growth rates 1mm/h – 1µm/h

Different growth material?

Rev.Adv.Mater.Sci. 21(2009) 134-138

GROWTH OF DIAMOND FILMS FROM TEQUILA

J. Morales[1,2], L.M. Apátiga[2] and V.M. Castaño[2]

[1]Facultad de Ciencias Físico Matemáticas, Universidad Autónoma de Nuevo León, Av. Universidad S/N, San Nicolás, Nuevo León, México 66450, Mexico
[2]Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de M... ...oulevard Juriquilla 3001, Santiago de Queretaro, Querétaro, México 76230 ...

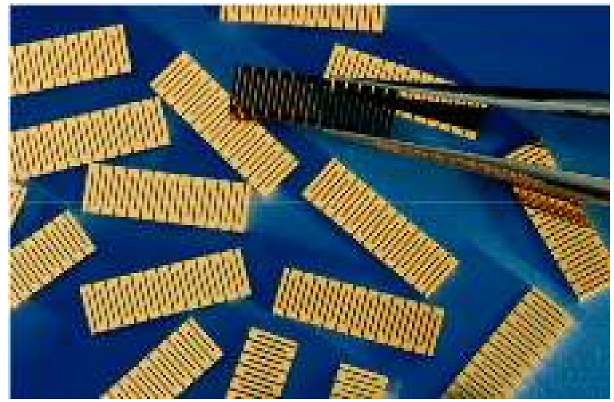
Received: February 19, 2009

Abstract. Diamond thin films were growth using Teq... ...injection Chemical Vapor Deposition (PLI-CVD) onto both silico... ...304 at 850 °C. The diamond films were characterized by Scanning Elec... ...M) and Raman spectroscopy. The spherical crystallites (100 to 400 nm) sh... ...acteristic 1332 cm^{-1} Raman band of diamond.

Ig-Nobel Prize 2009
www.ignobel.org

CVD diamond applications

Ultrasharp wear resistant diamond knife



Flexible CVD diamond heatspreaders

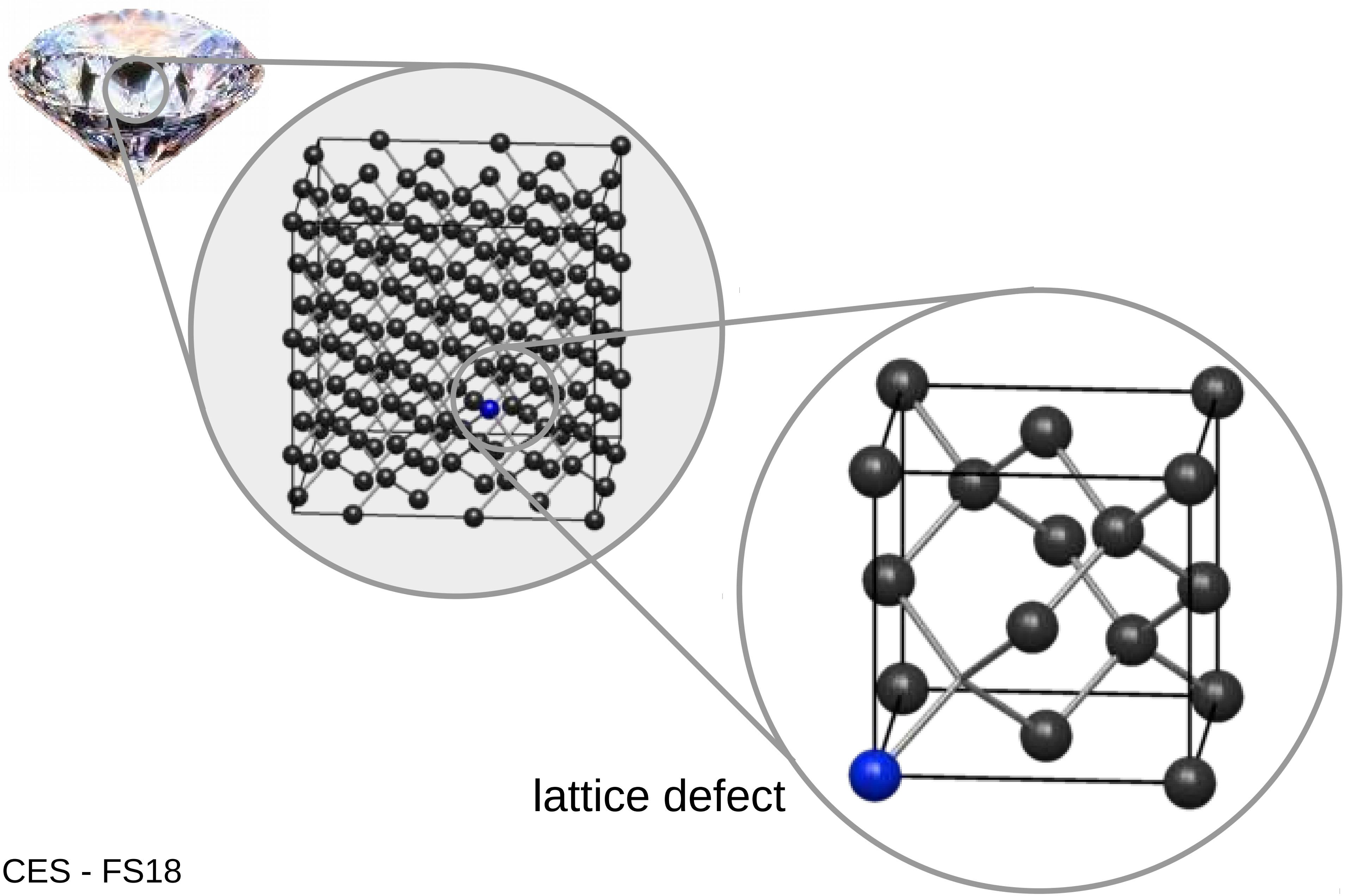
CVD diamond laser windows

CVD diamond window in UHV flange

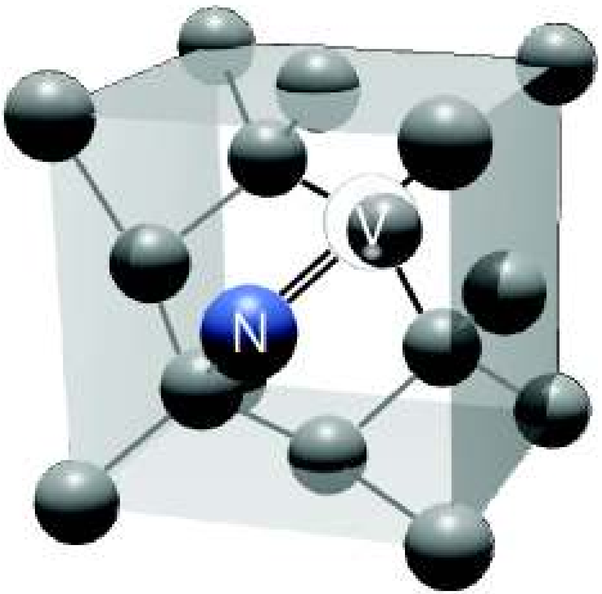
Decorative CVD diamond dial

CVD diamond anchor wheel

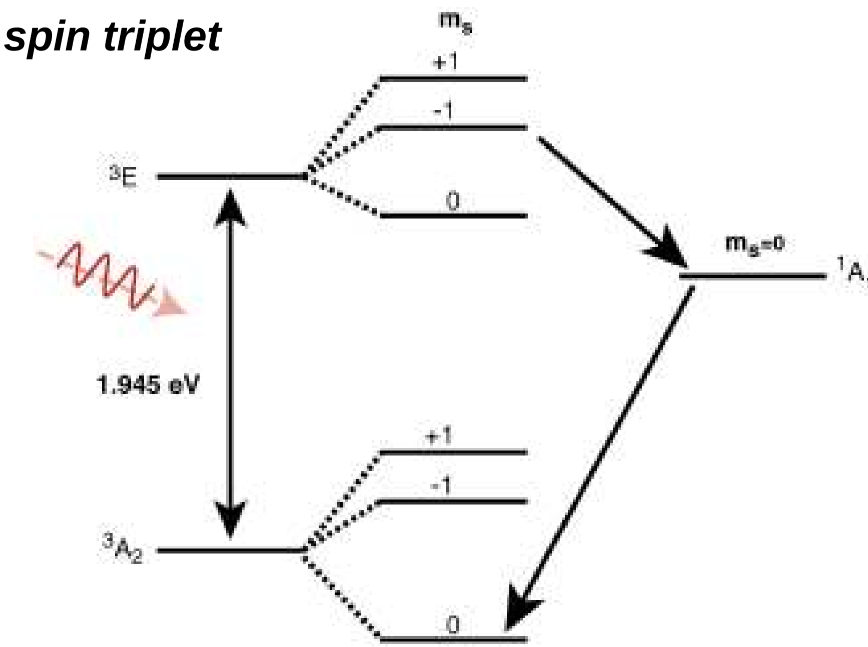
Color of diamonds, defect centers



Defects in Diamonds
Nitrogen-vacancy centers (NV)



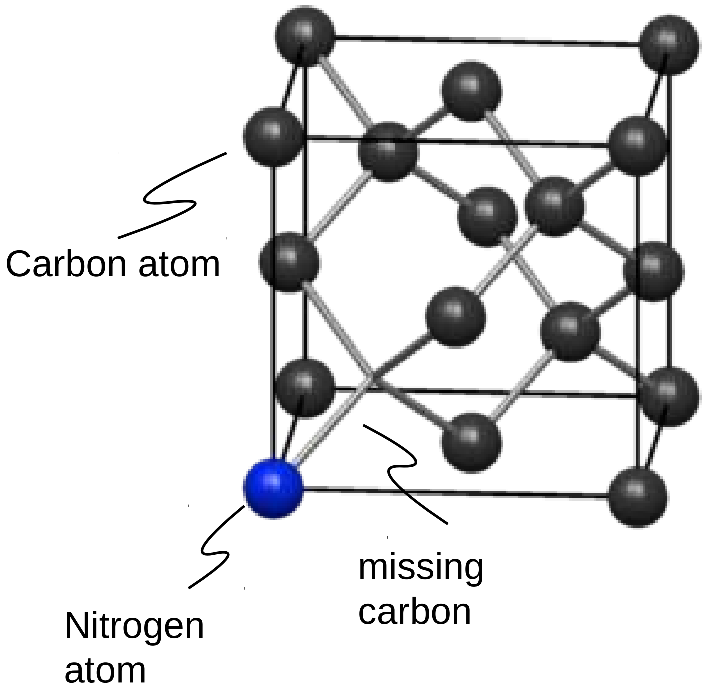
Ground state spin triplet



- **Color centers** : Nitrogen, boron...
- Diamond structure = mechanical, electronic and magnetic shield for the NV centers
- Long-life spin states events even at RT -> quantum computing with NV^{-1}
- Optical properties (single photon source) -> application in photonics and bio-medical imaging

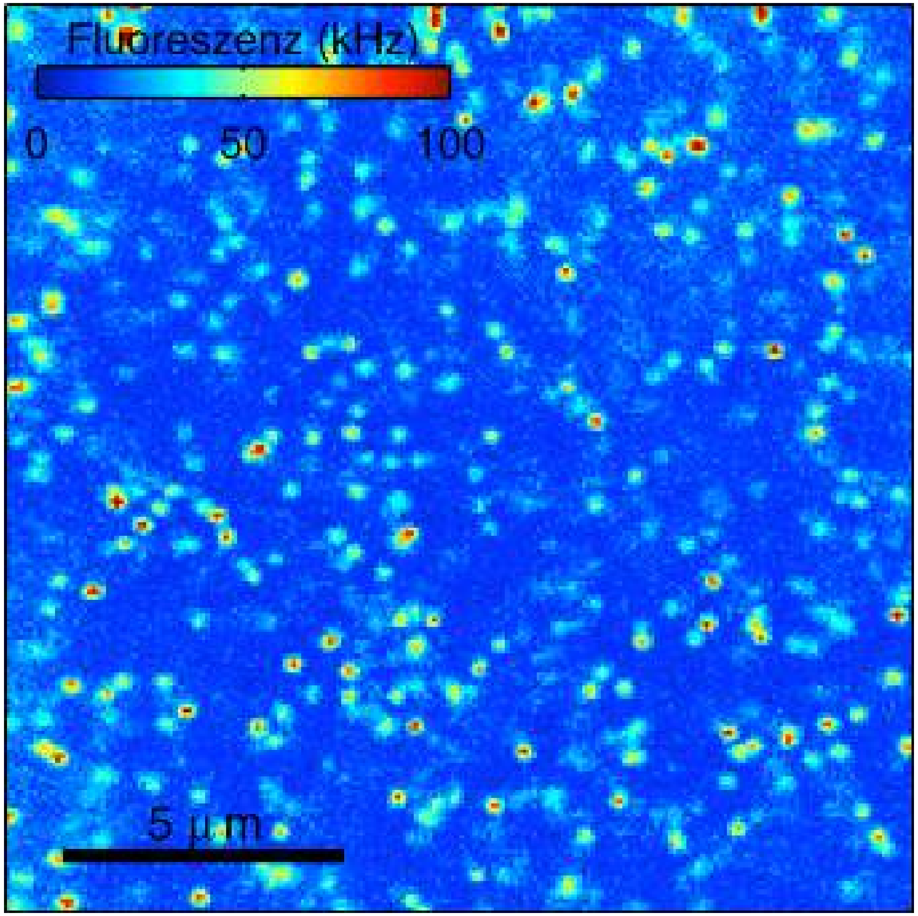
J.R. Weber et al. *PNAS*, **17**, 85158518, (2010)
Alivisatos Paul, *Nature Biotech.*, **22**, 4752, (2004)

NV-centers in diamond

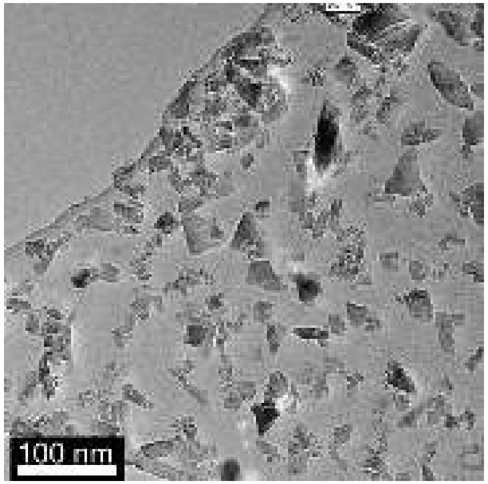


The vacancy can be occupied by an electron with a spin!

NV- fluorescence

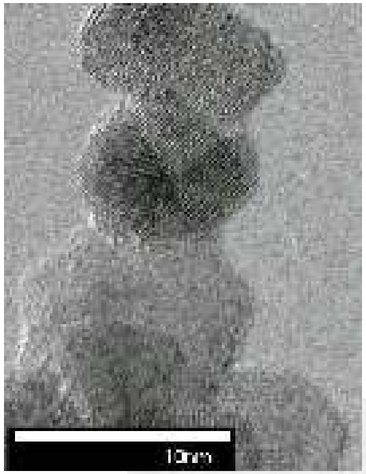


Nanodiamonds



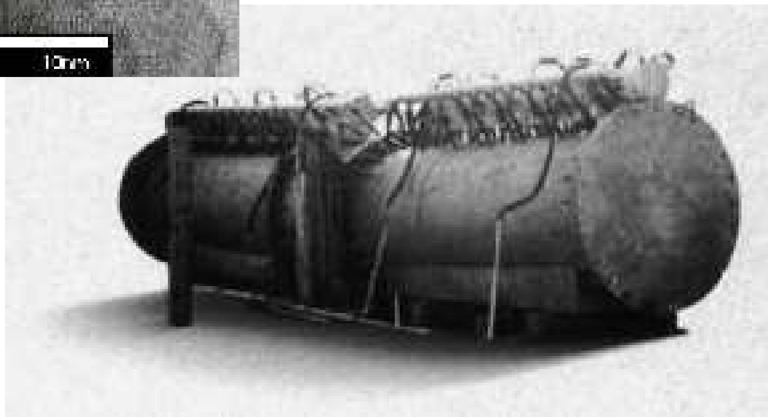
HPHT: High Pressure High Temperature

- by milling of diamond microcrystals, various sizes and shapes
- better crystallinity, less non-diamond phase than UDD



UDD: Ultradispersed Detonation Diamond

- from oxygen-deficient explosions in a reactor
- typical size 3-8 nm, given by explosion conditions, „spherical“ shape
- obtained from the detonation soot (~60%), needs purification and deaglomeration
- various surface functional groups, poor crystallinity (lattice defects)

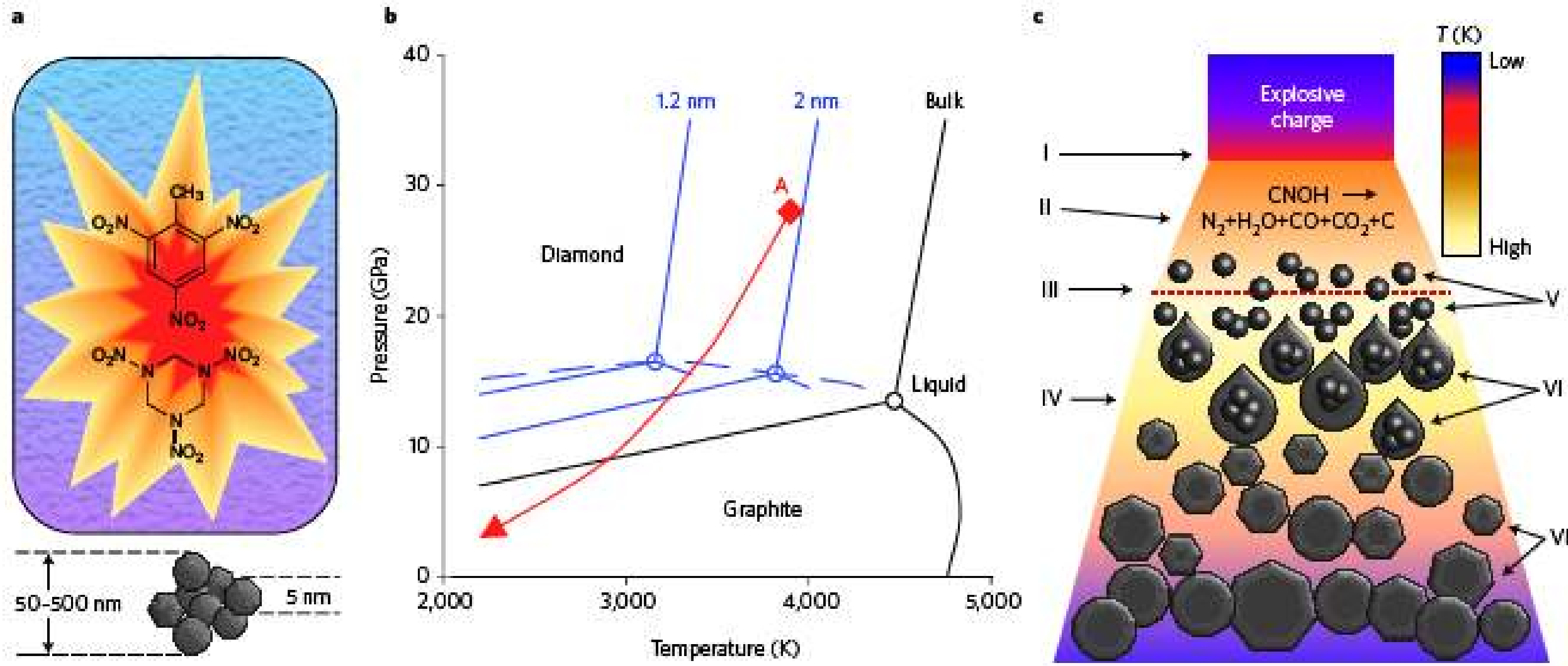


A. Krueger, J. Mater. Chem., 2008, 18, 1485–1492
K. Iakoubovskii et al. Nanotechnology 19 (2008) 155705

Synthesis of nanodiamonds
Detonation Technique (RDX+TNT)

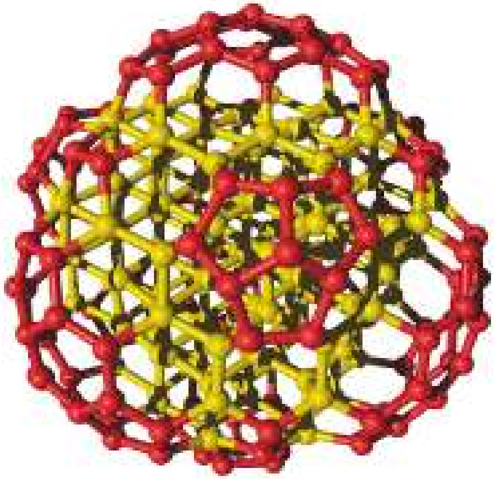
TNT

RDX



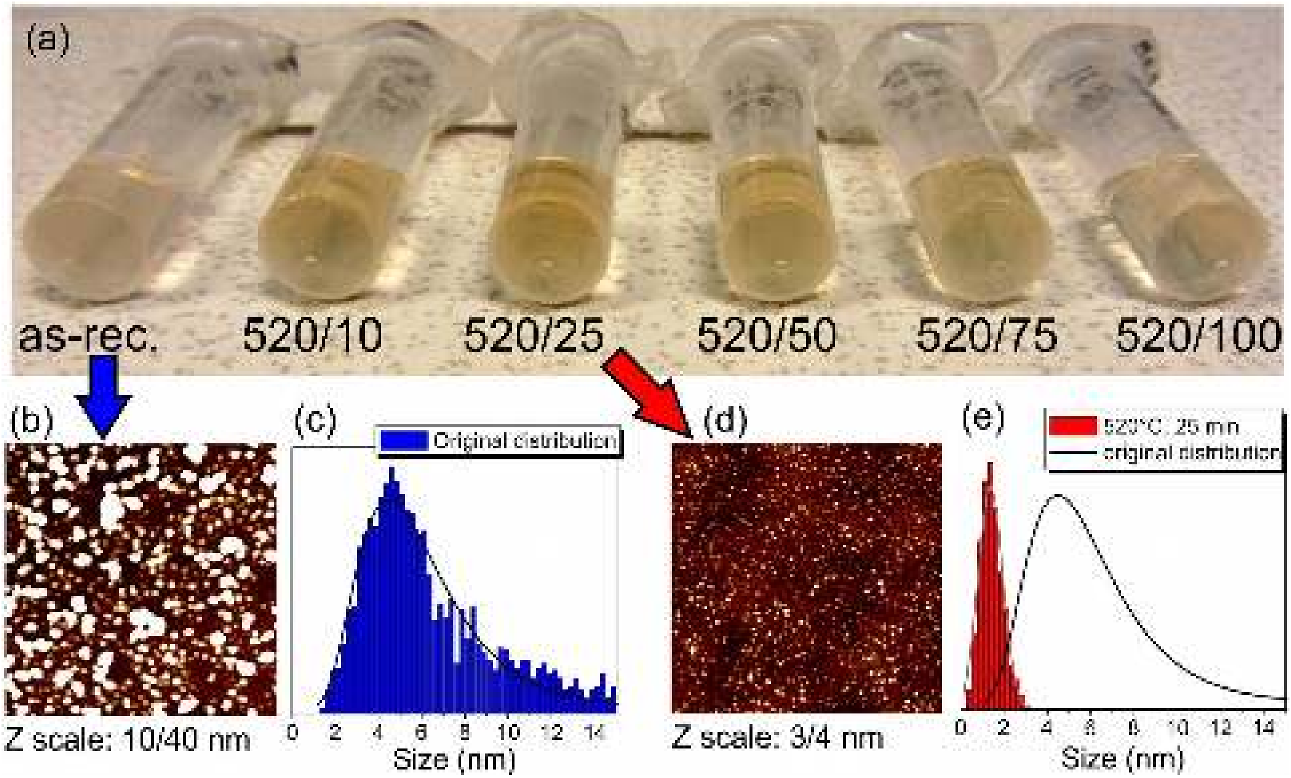
Bucky-diamond structure ?

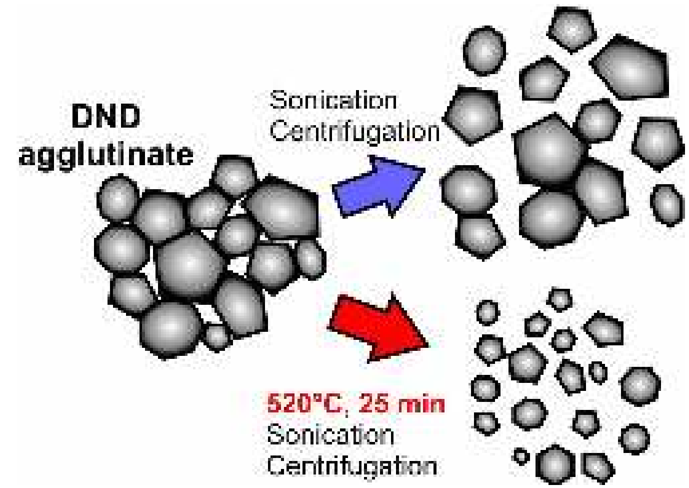
- Coexistence of ***diamond structure*** (core) and ***graphite-like reconstructions*** (surface)?

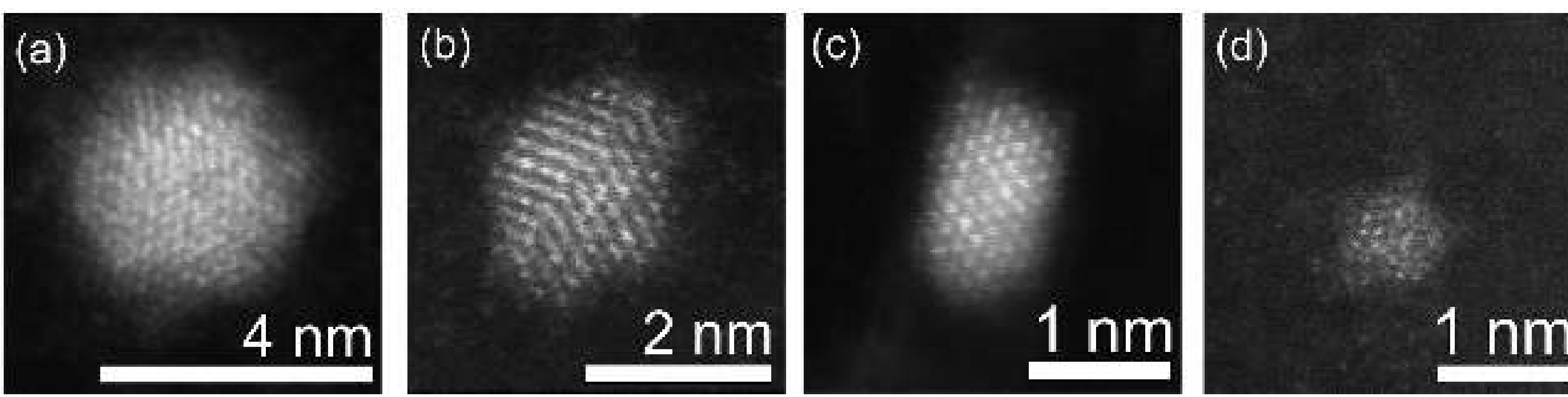


V. N. Mochalin *et al., Nature Nanotechnol.* , **7**, 11-16 (2012)
J.-Y. Raty, G. Galli, Nature Mat., **2**, 792–795 (2003)

Molecular-sized DNDs

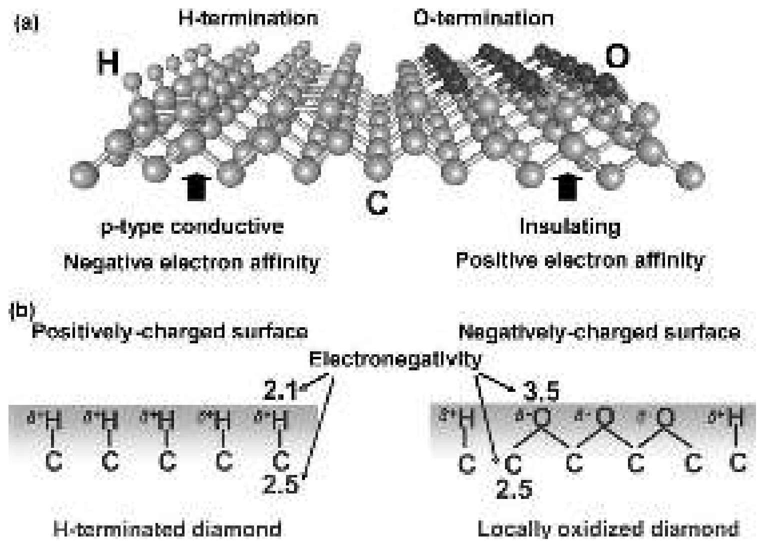


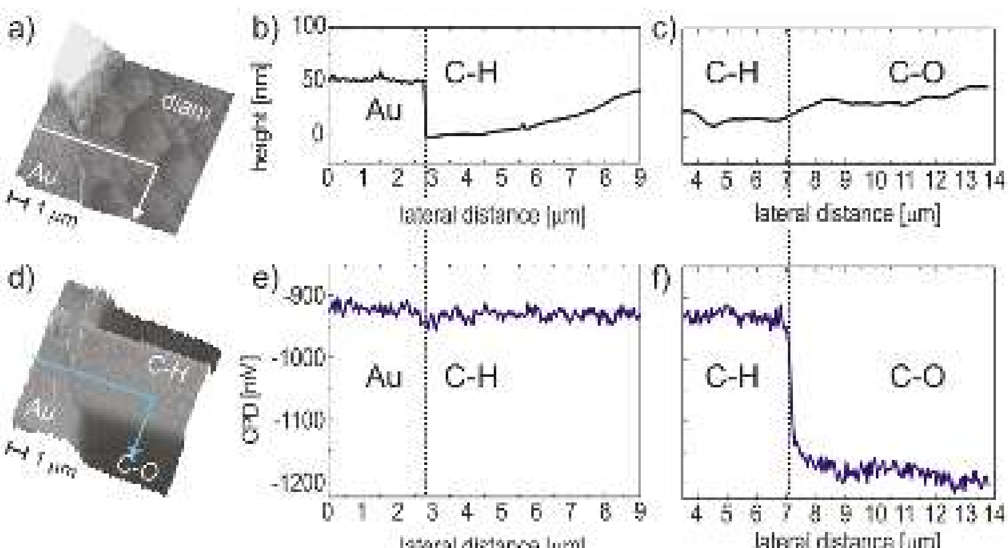


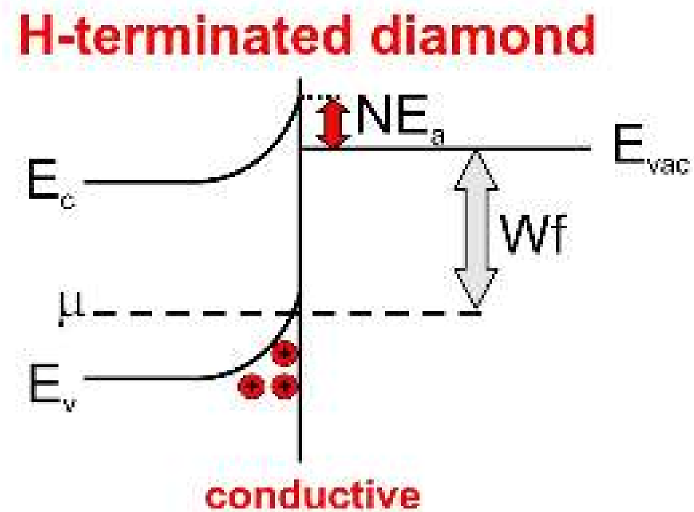


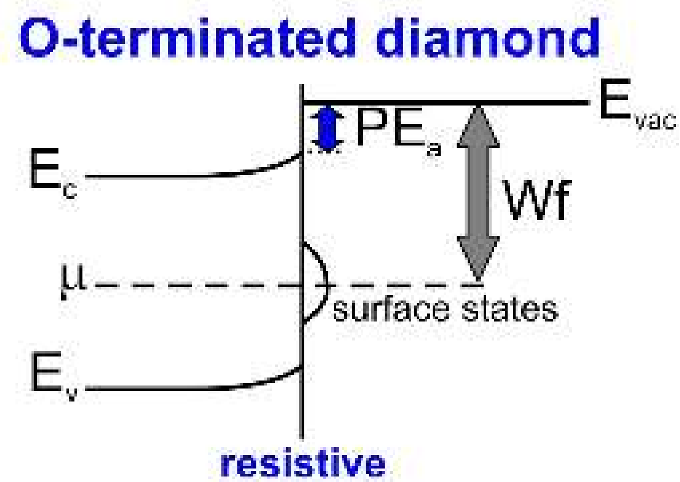
S. Stehlik et al., Scientific Reports 6, 38419 ,(2016).

Surface of H-/O-diamond



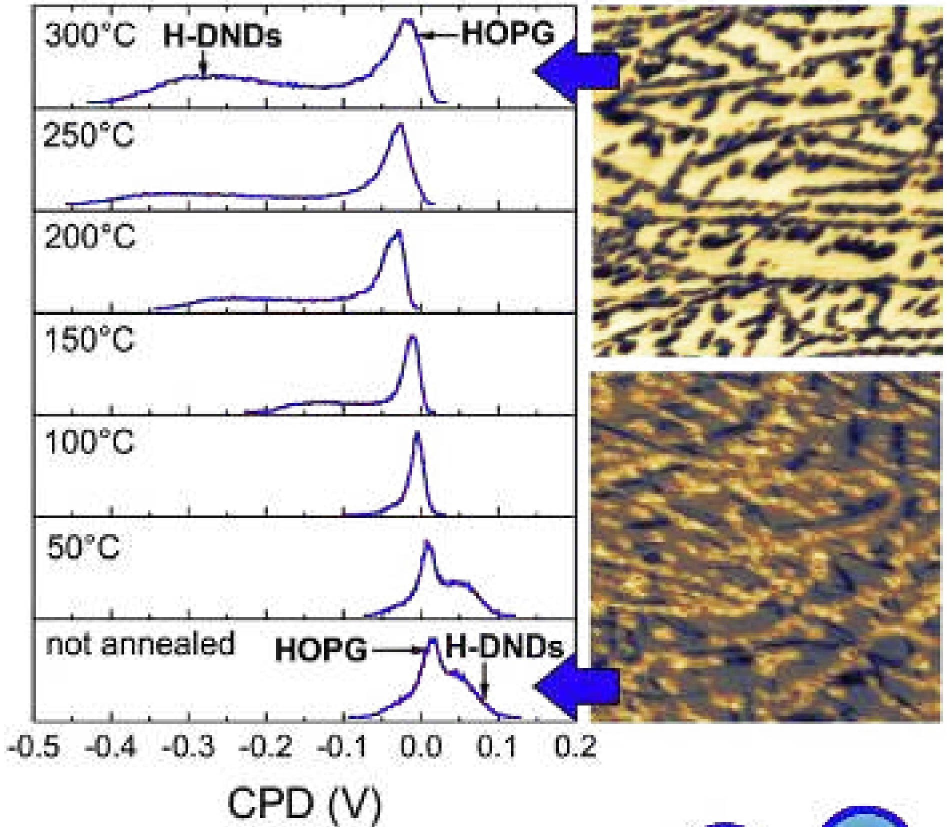


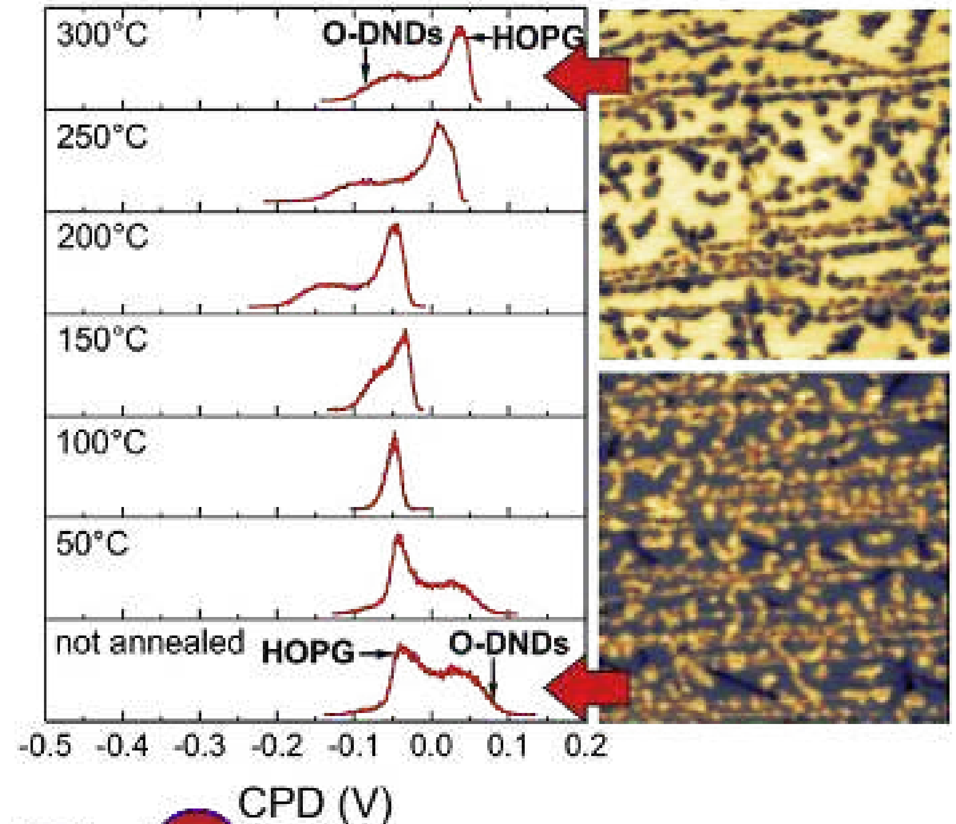




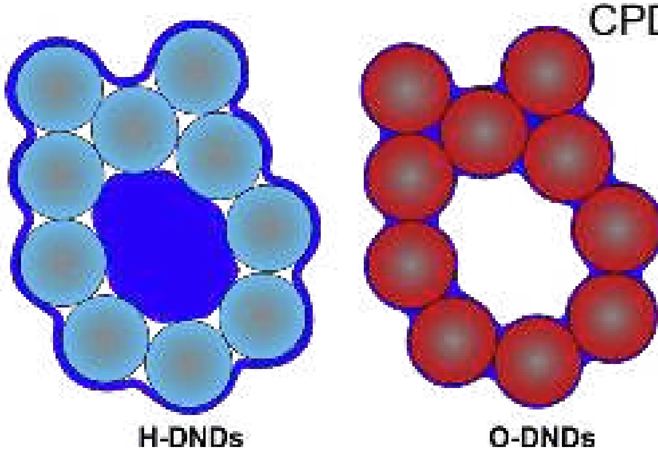
M. Tachiki et al. Surface Science 581 (2005) 207–212
B. Rezek et al. APL 82 (2003) 2266

Water Interaction with H- and O-DNDs





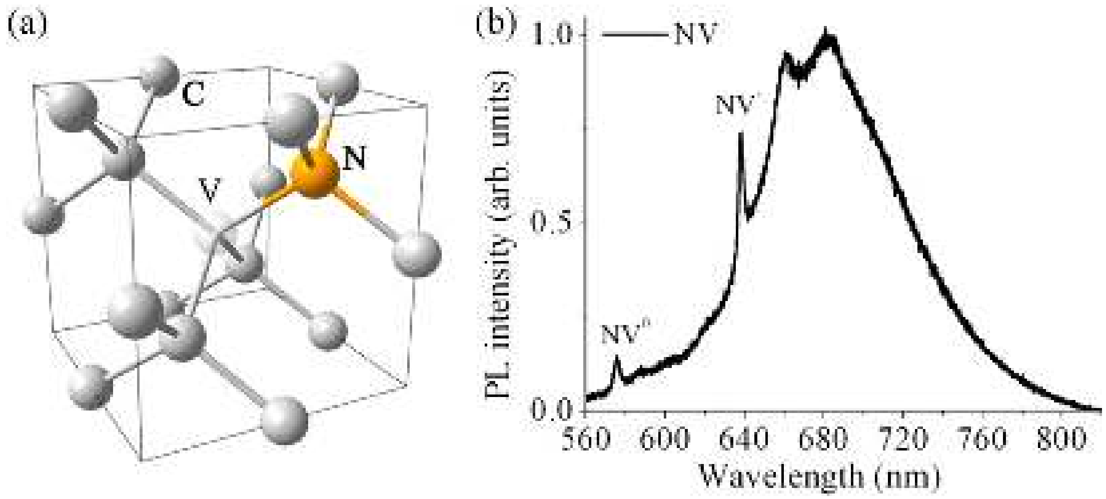
- hydrophobic interaction
- formation of weakly bound H_2O
- additional H_2O nanodroplets

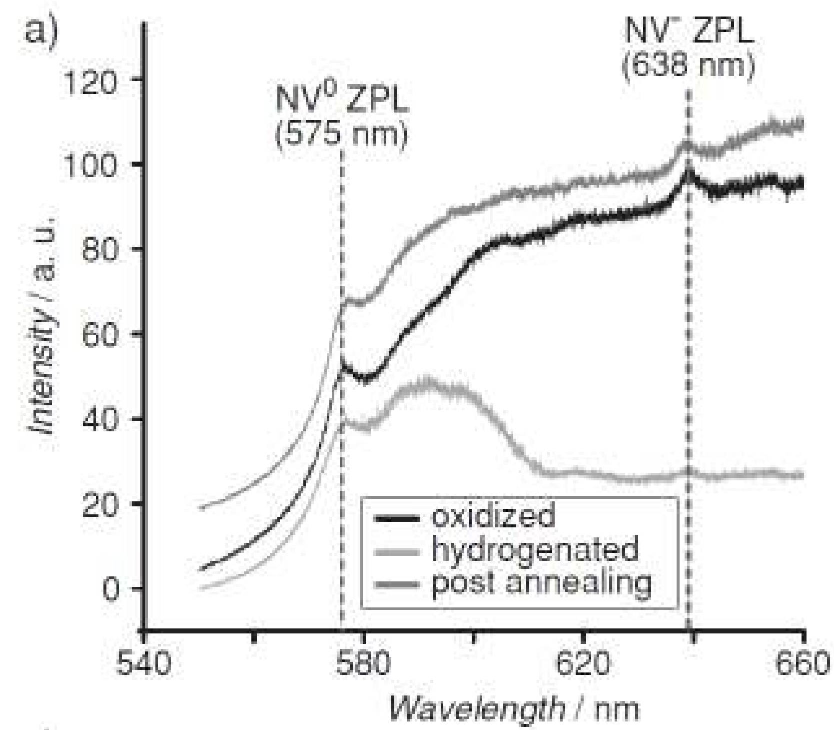


- hydrophilic interaction
- formation of strongly bound surface H_2O

S.Stehlik, Th. Glatzel, et al., Diamond and Related Materials 63, 97-102 ,(2016).

Surface influence on NV centers



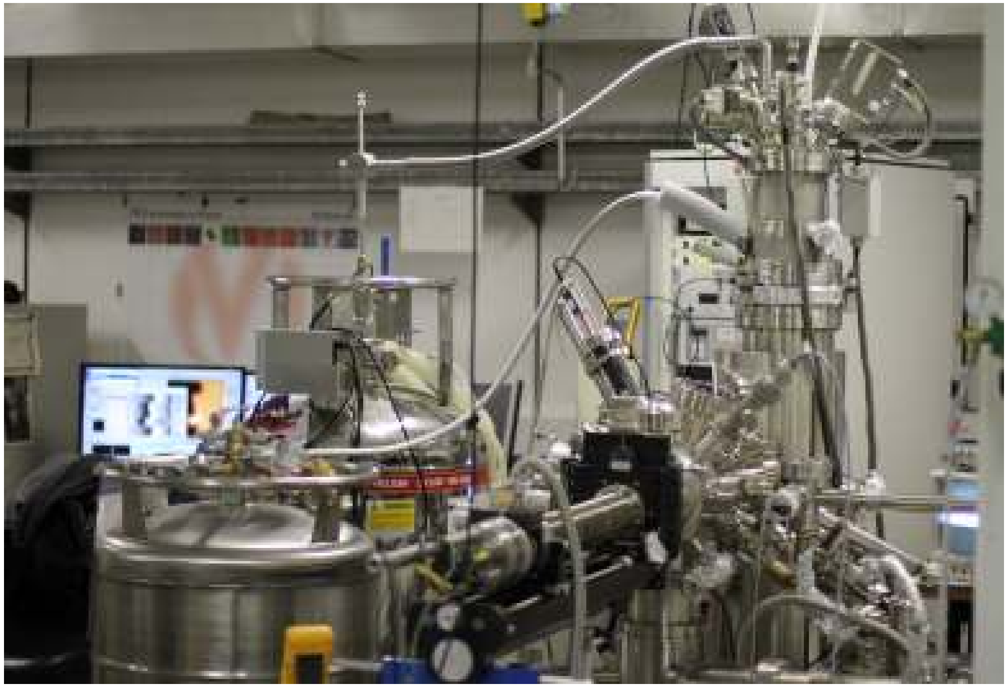


NV center point defect, broadly studied

- by ion implantation and subsequent annealing
- two charge states NV^0, NV^-
- NV^- single photon source, suitable for spintronics
- red emission for bio-imaging
- NV^0/NV^- ratio controlled by surface termination
- detected even in UDD nanoparticles

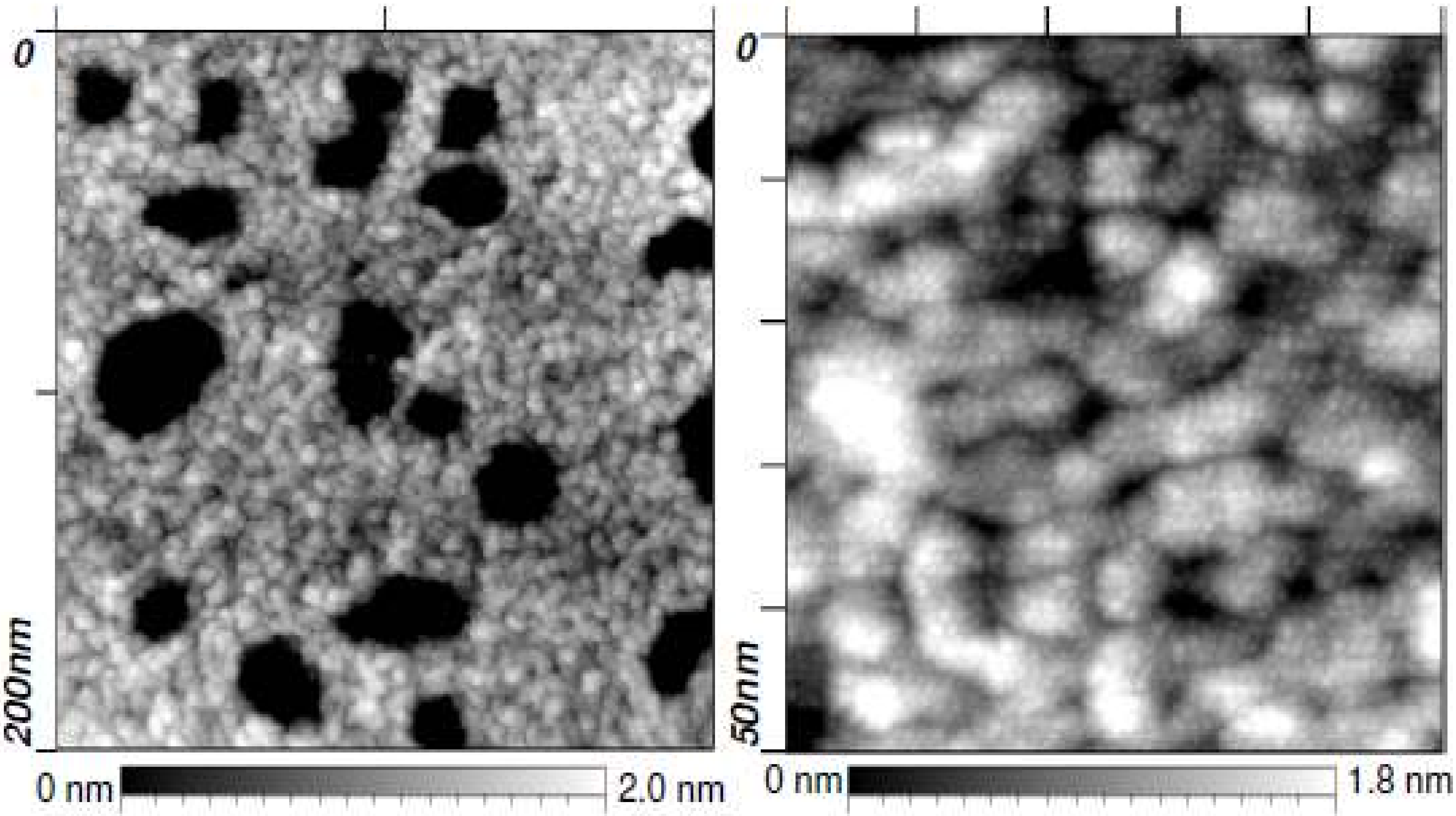
I. Aharonovich et al. Rep. Prog. Phys. 74 (2011) 076501
V. Petráková et al. Adv. Funct. Mater. 2012, 22, 812-819

Tuning fork based LT-AFM/STM



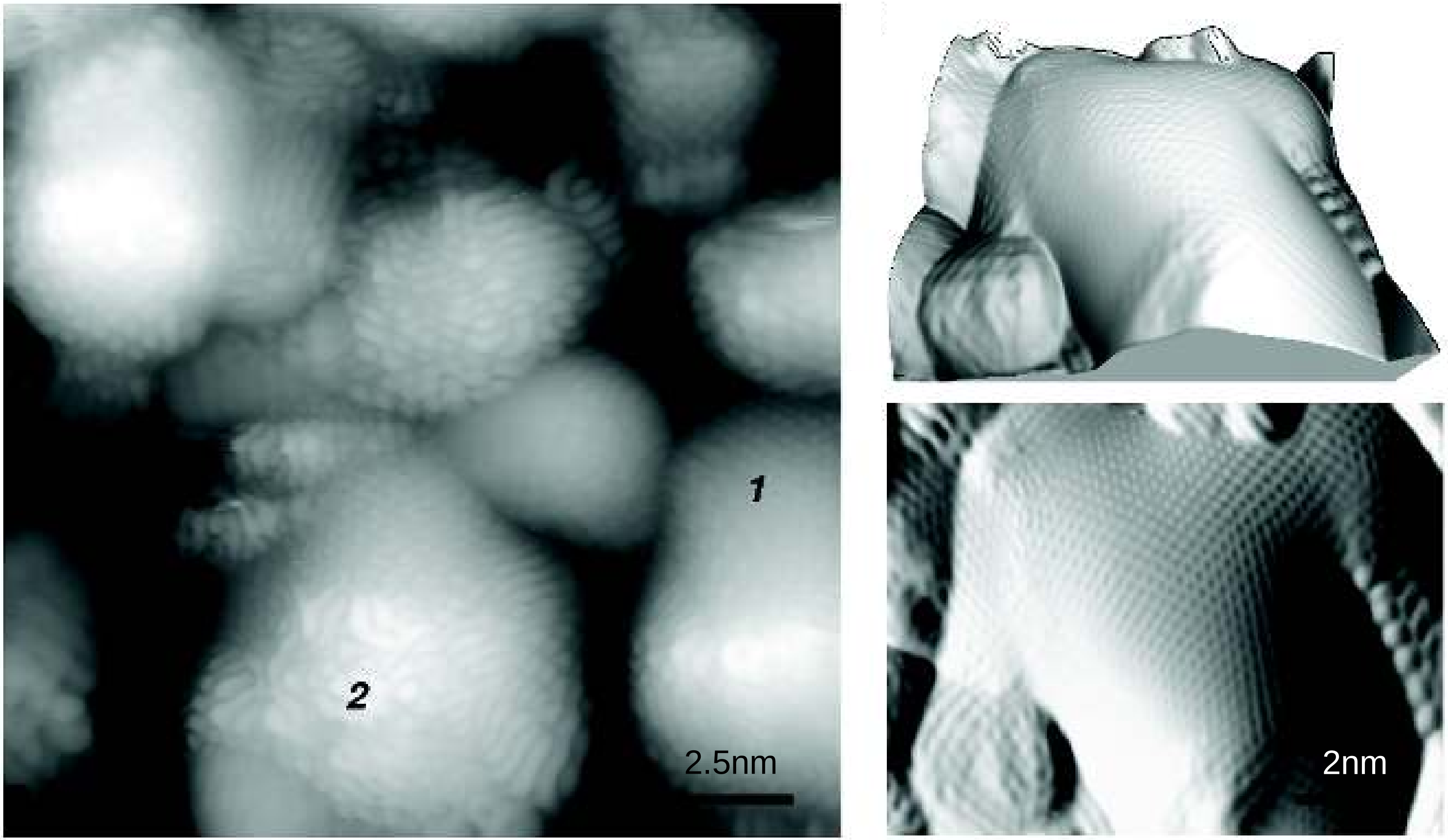
- **qPlus tuning fork** with separate wire at low temperature 4K
- Preparation of metals, oxides and semi-conductors
- Molecular evaporator, spray deposition technique
- **Optical excitation from an ex-situ LED source** (4 wavelengths, P = 10 mW/cm^2)

Sub-monolayer of nanodiamonds/HOPG
Electrophoresis deposition technique



L. Schimidlin *et al.*, Appl. Phys . Lett. **101**, (2012)
V. Pichot *et al.*, J. Phys Chem. C **114**, 10082 (2010)

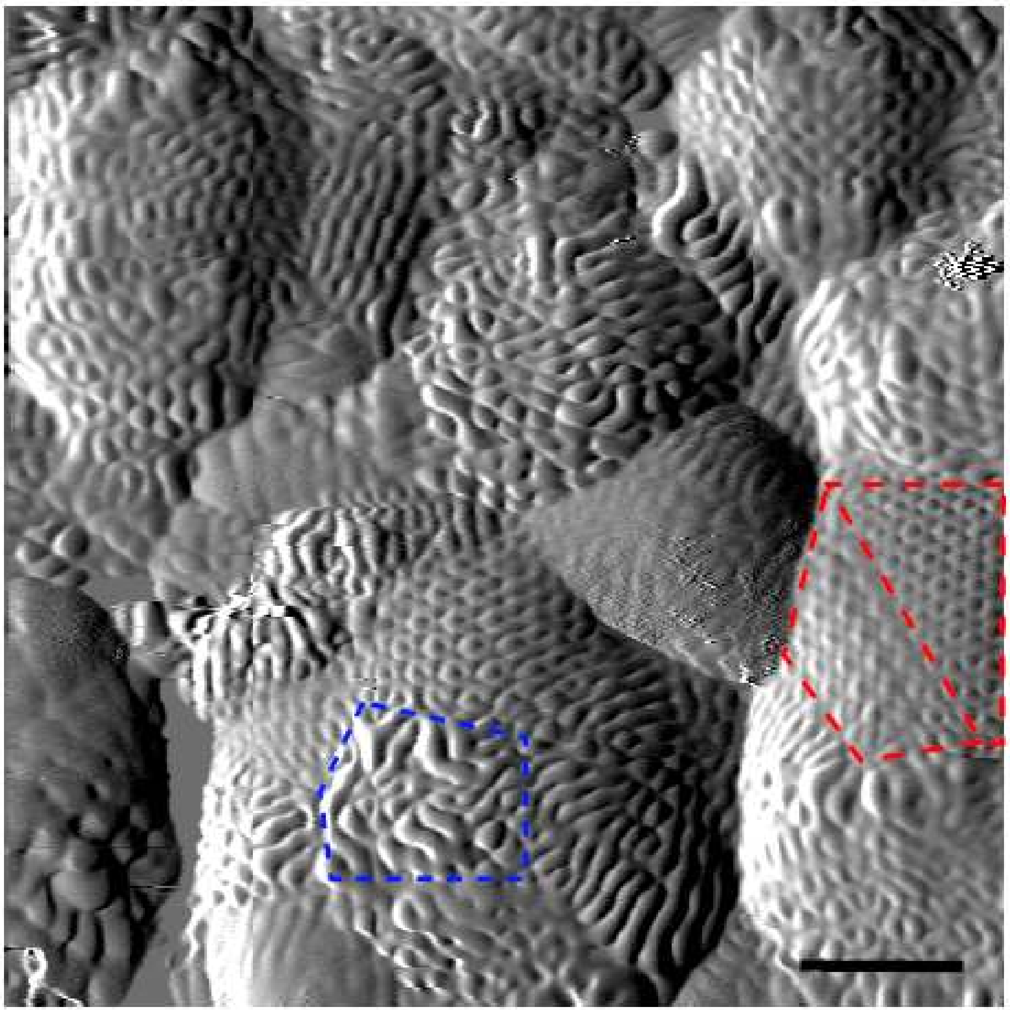
Surface structure of nanodiamonds



It = 20pA, V = -1.8 V

R. Pawlak et al.,Nano Lett. 13, 5803–5807, (2013).

Surface structure of nanodiamonds



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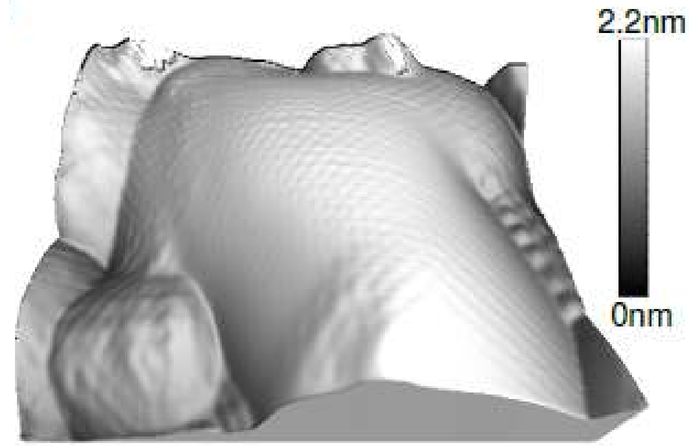
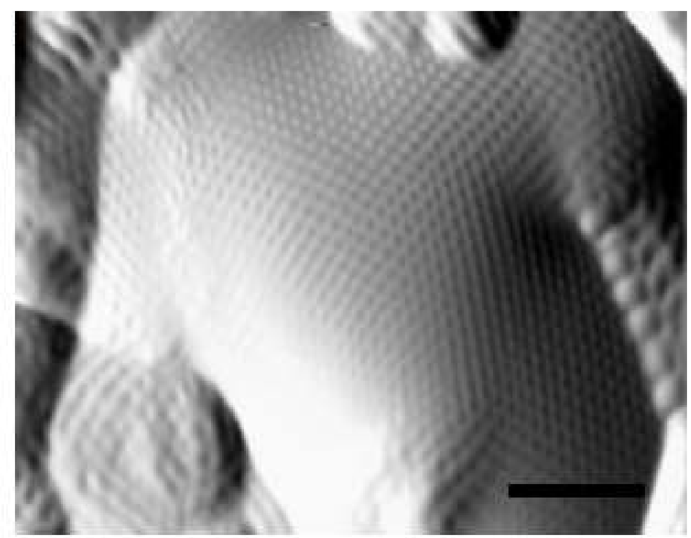
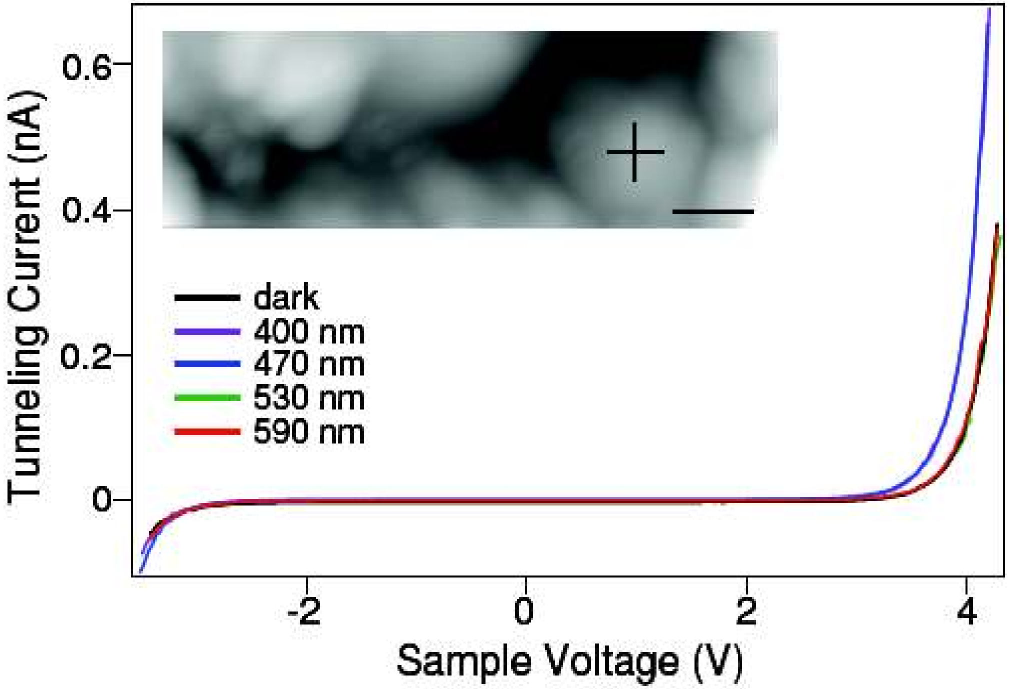
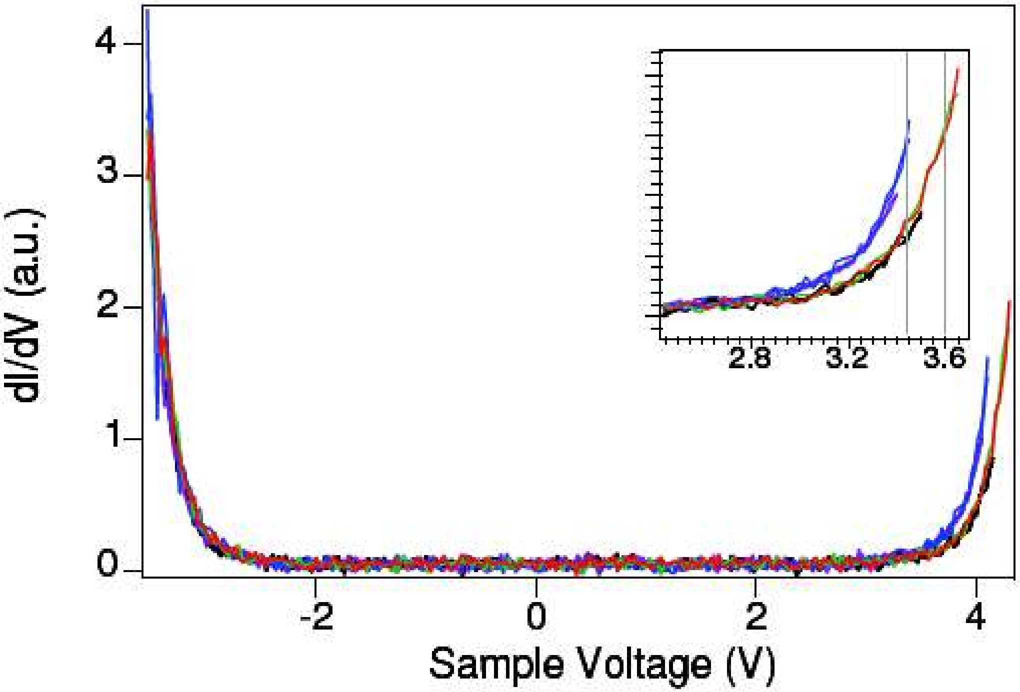




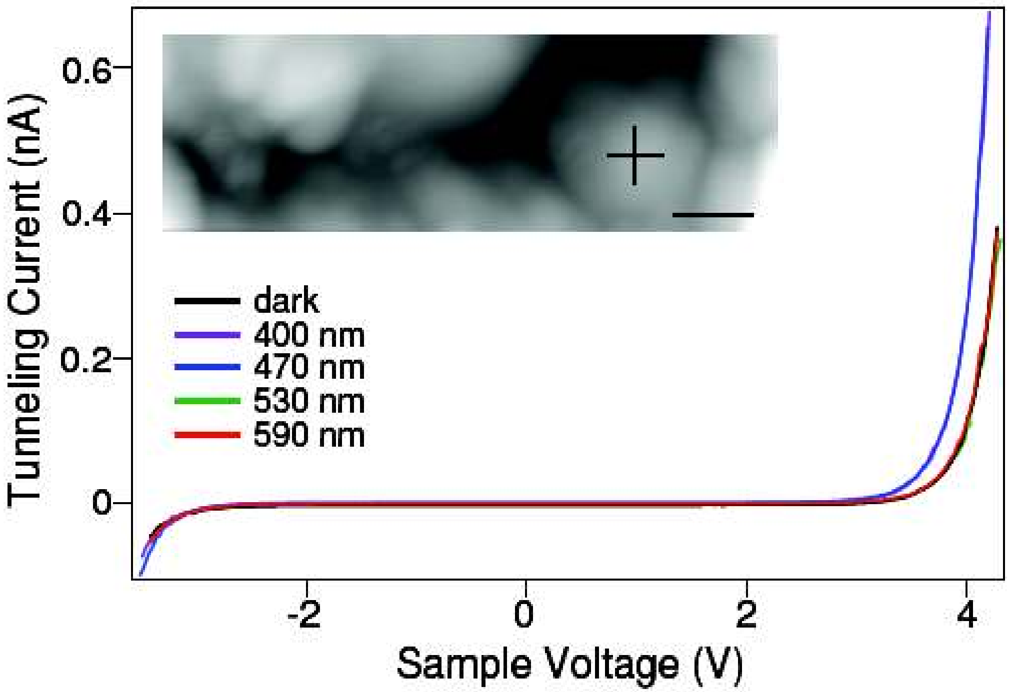
- Facets with C(111) structure
- Graphitic defects.

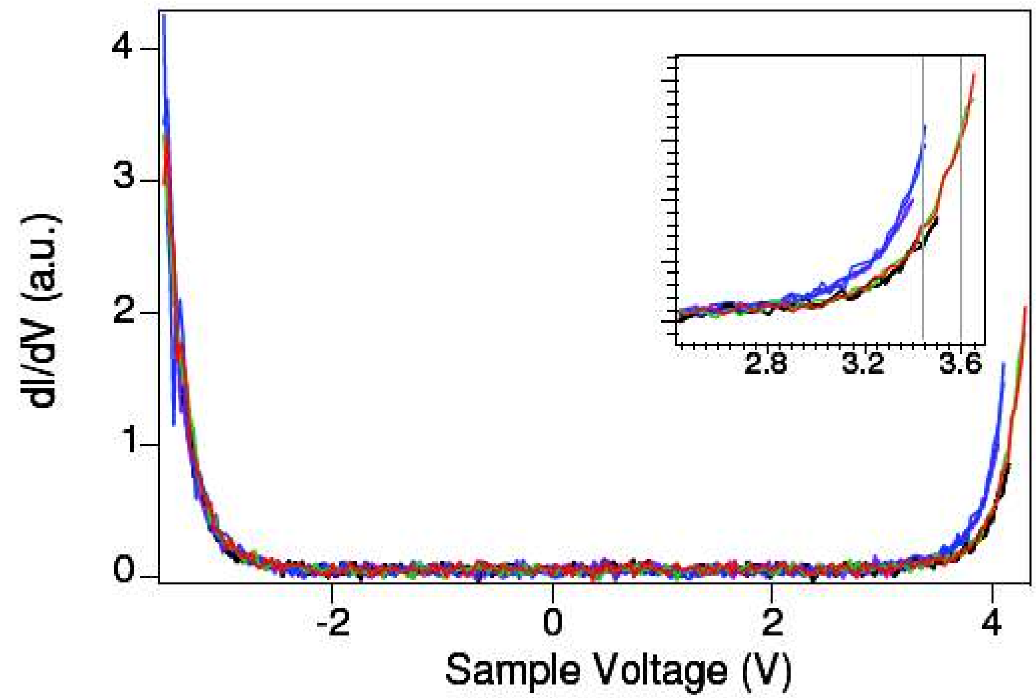
Light-assisted tunneling spectroscopy



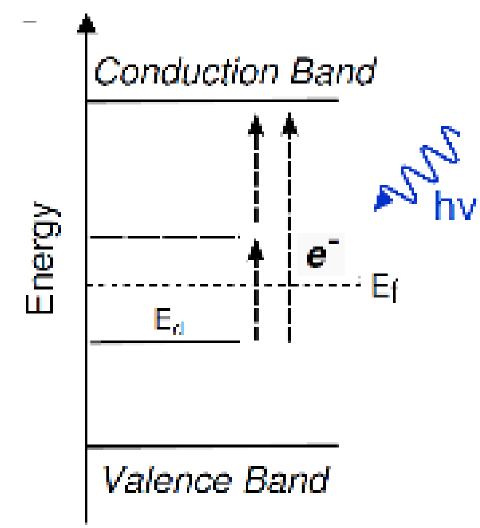


Light-assisted tunneling spectroscopy

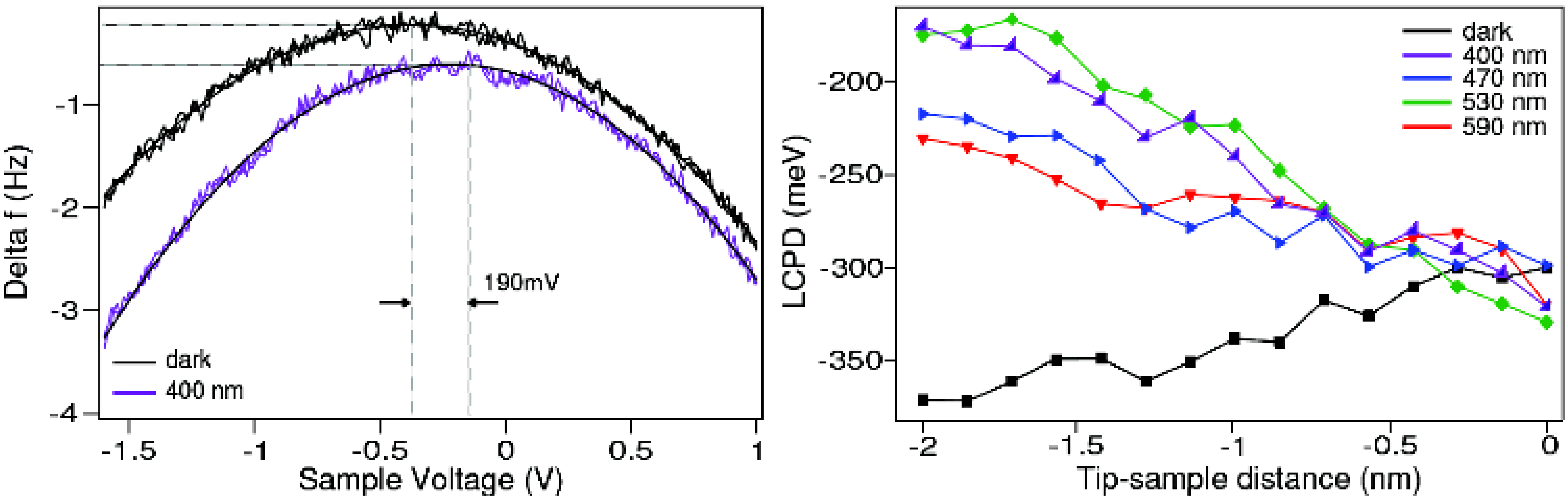




- Band gap of 6-6.5 eV → ***Diamond !***
- ***Variation of the conduction band*** under illumination (λ < 500 nm)
- Nanodiamonds are n-doped
- Sub-band gap illumination (3 eV maximum) = ***charge transfer from sub-surface defects.***



Kelvin spectroscopy under illumination

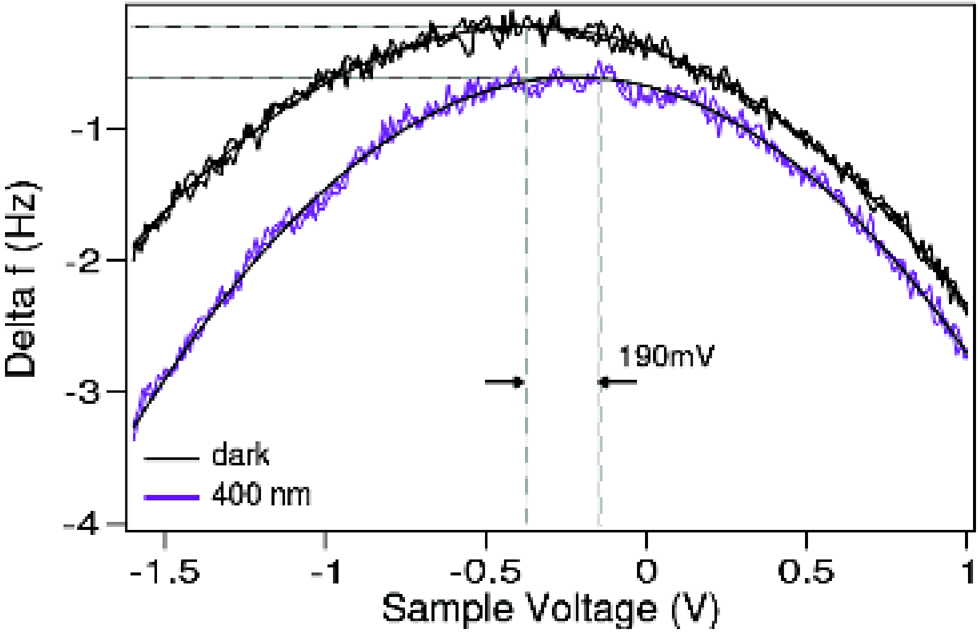


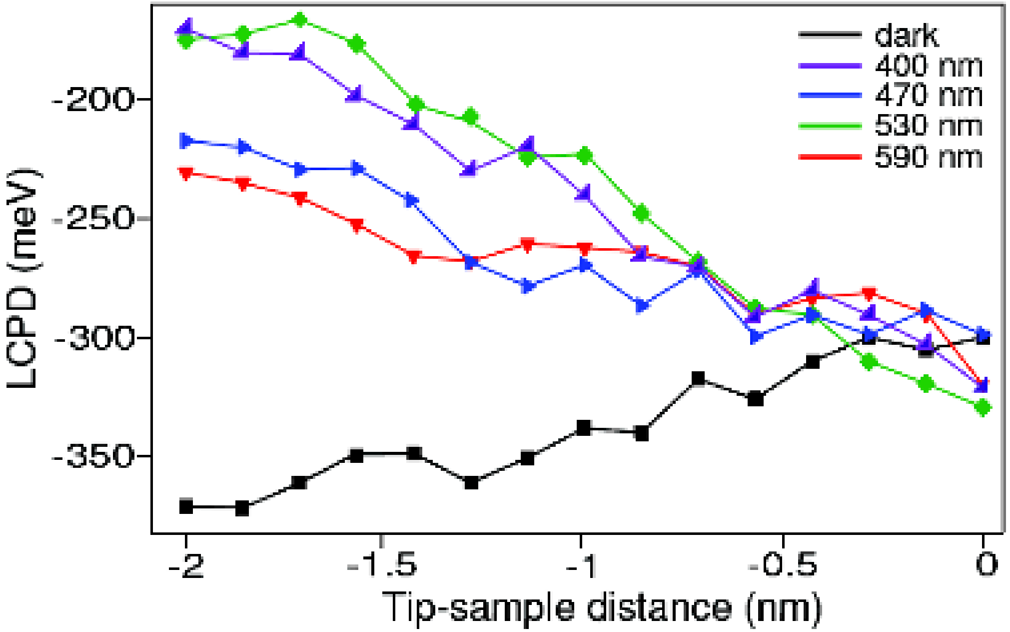
Φ[C(111)] = 4.7 eV, Φ[Cu(111)] = 4.95 eV

=> ***Absolute Contact Potential Difference (CPD) = $\Phi_{tip} - \Phi_{sample}$ = -250 meV***

C. Barth et al., Phys. Rev. Lett., **98**, 136804 (2007)
L. Gross et al., Science, **325,** 1110 (2009)

Kelvin spectroscopy under illumination





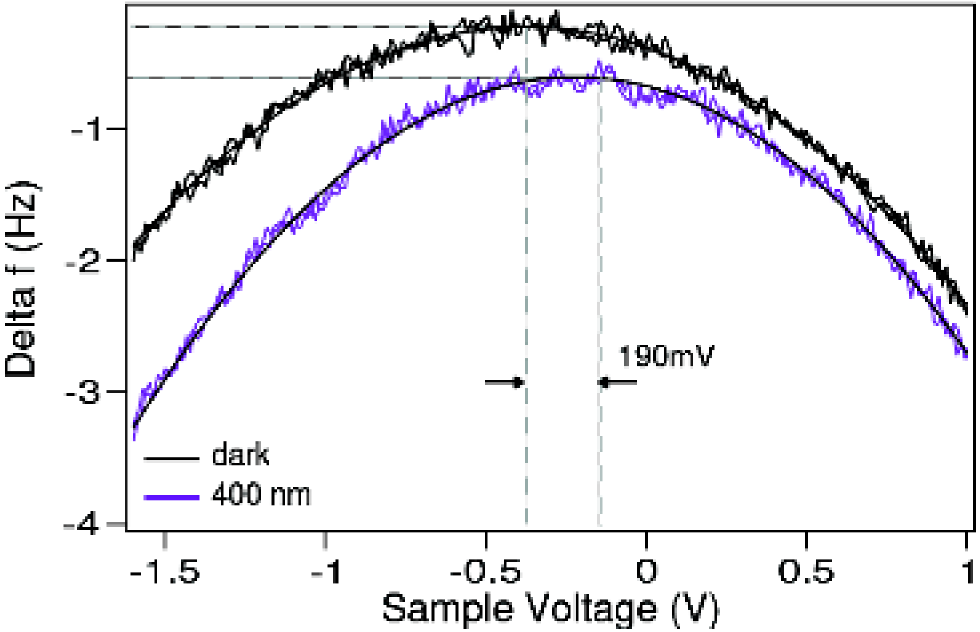
Φ[C(111)] = 4.7 eV, Φ[Cu(111)] = 4.95 eV
=> ***Absolute Contact Potential Difference (CPD) =*** $\Phi_{tip} - \Phi_{sample}$ ***= -250 meV***

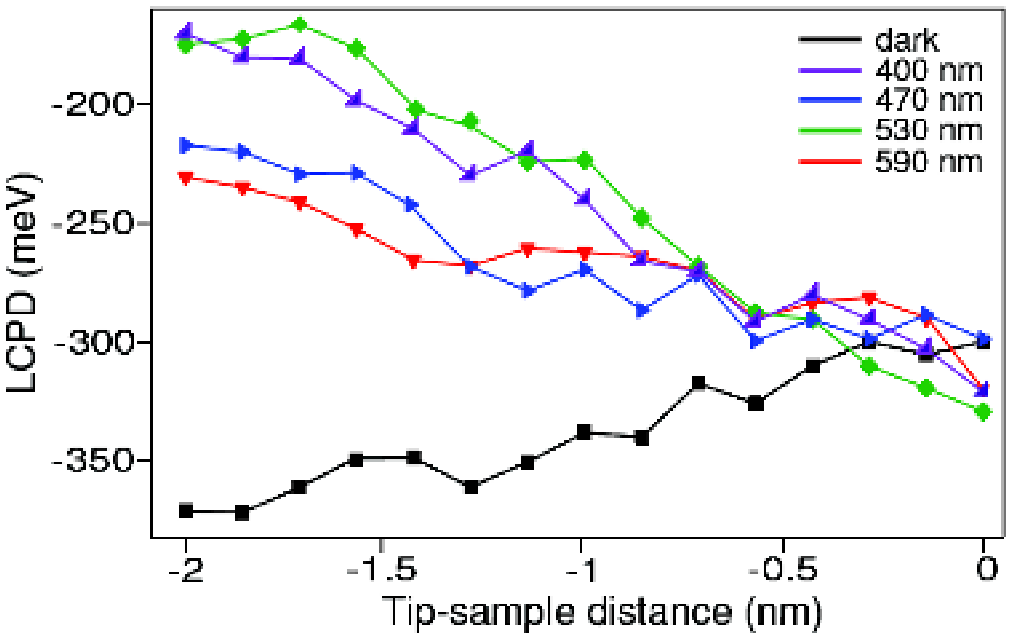
- Long-range electrostatic force regime = ***surface photo-voltage*** (band bending)

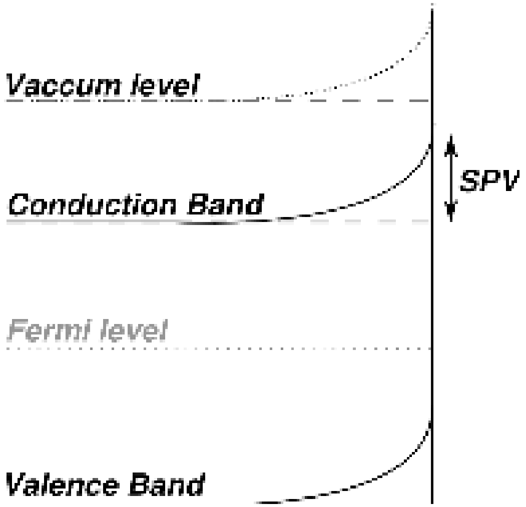
- Short-range E_{ts} force regime = ***sensitive to charges of NV centers***

C. Barth et al., Phys. Rev. Lett., **98**, 136804 (2007)
L. Gross et al., Science, **325,** 1110 (2009)

Kelvin spectroscopy under illumination





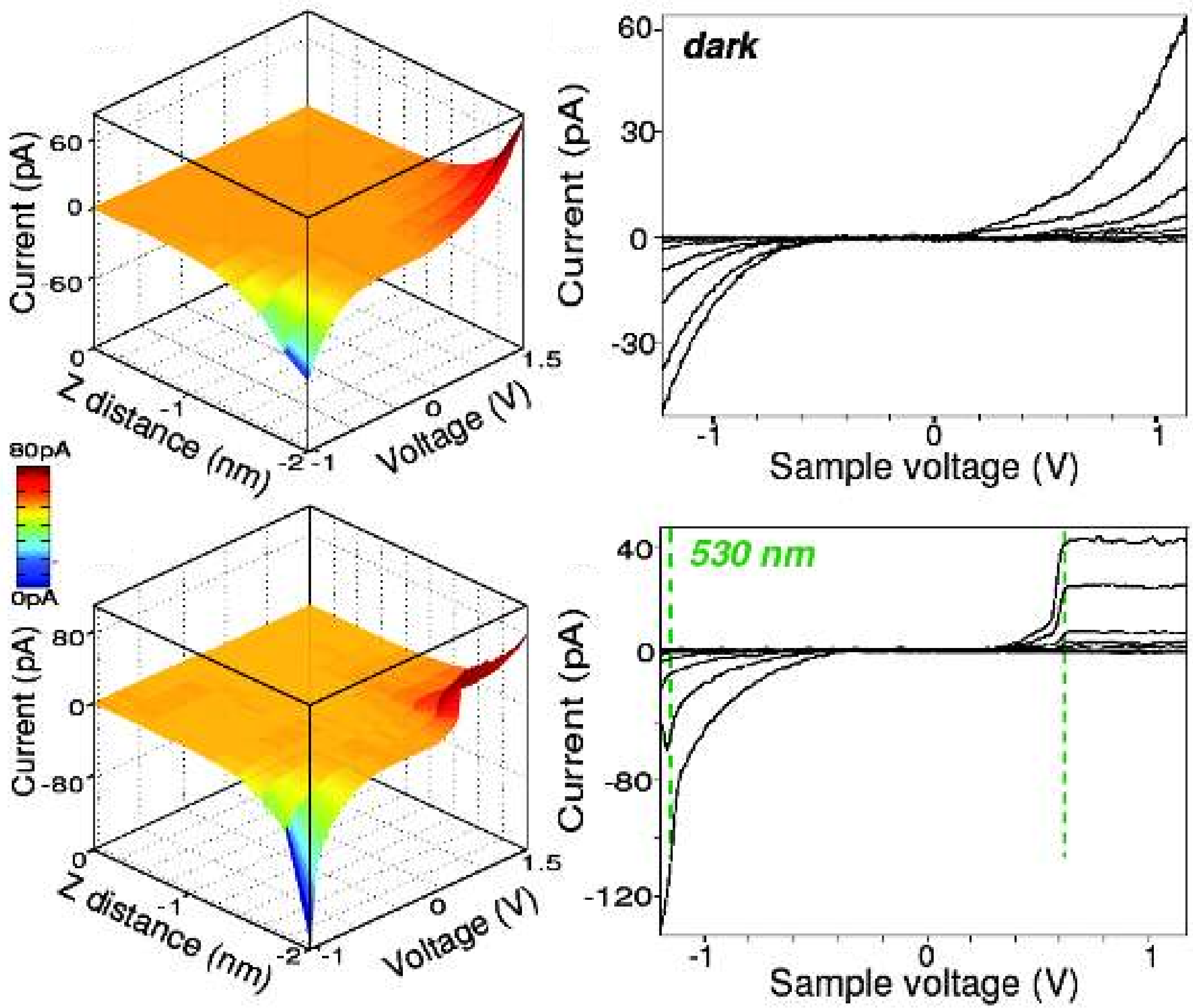


Φ[C(111)] = 4.7 eV, Φ[Cu(111)] = 4.95 eV
=> ***Absolute Contact Potential Difference (CPD) =***
$\Phi_{tip} - \Phi_{sample}$ **= -250 meV**

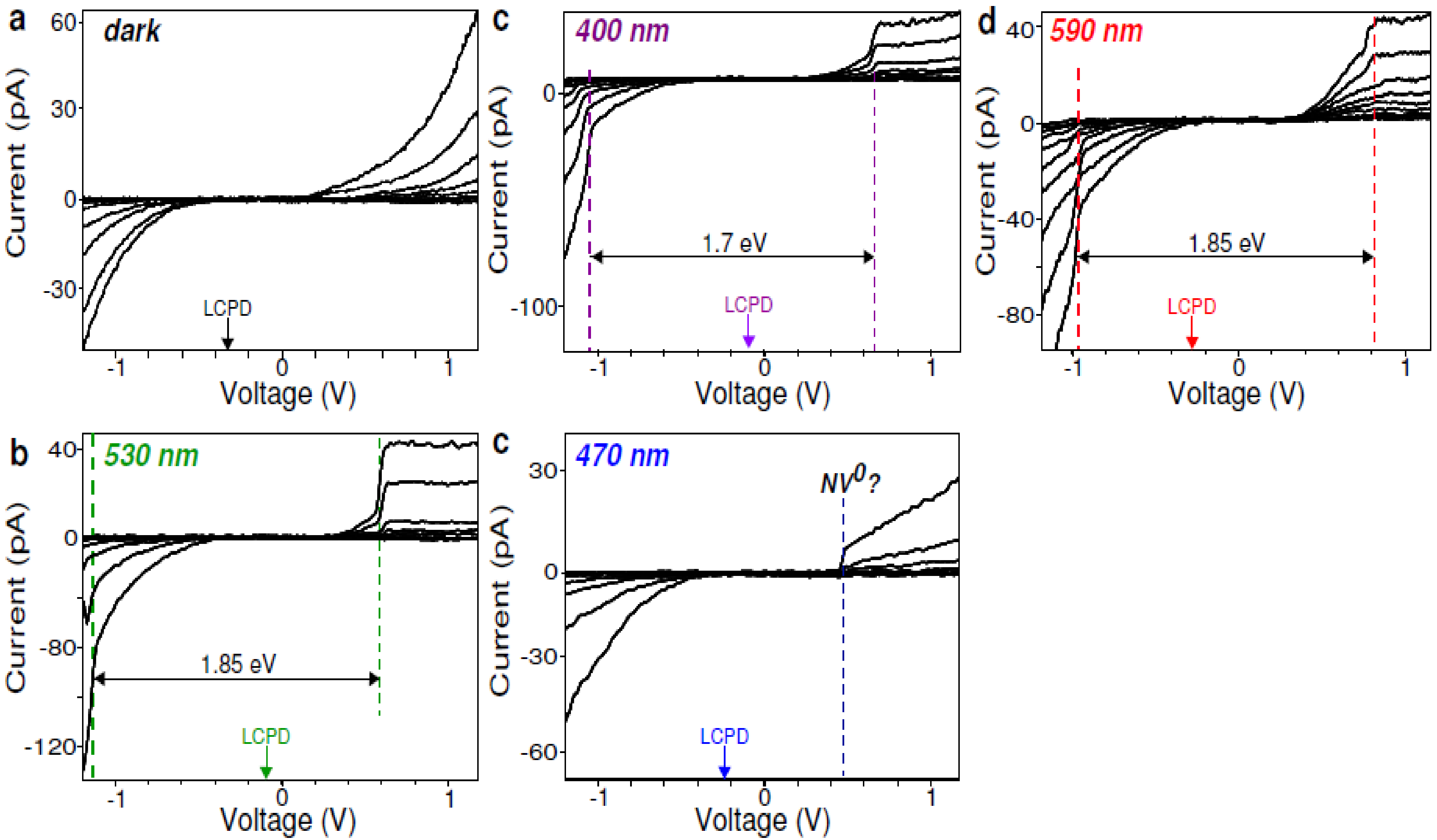
If SPV effect, LCPD should become more negative under Illumination...

C. Barth et al., Phys. Rev. Lett., **98**, 136804 (2007)
L. Gross et al., Science, **325,** 1110 (2009)

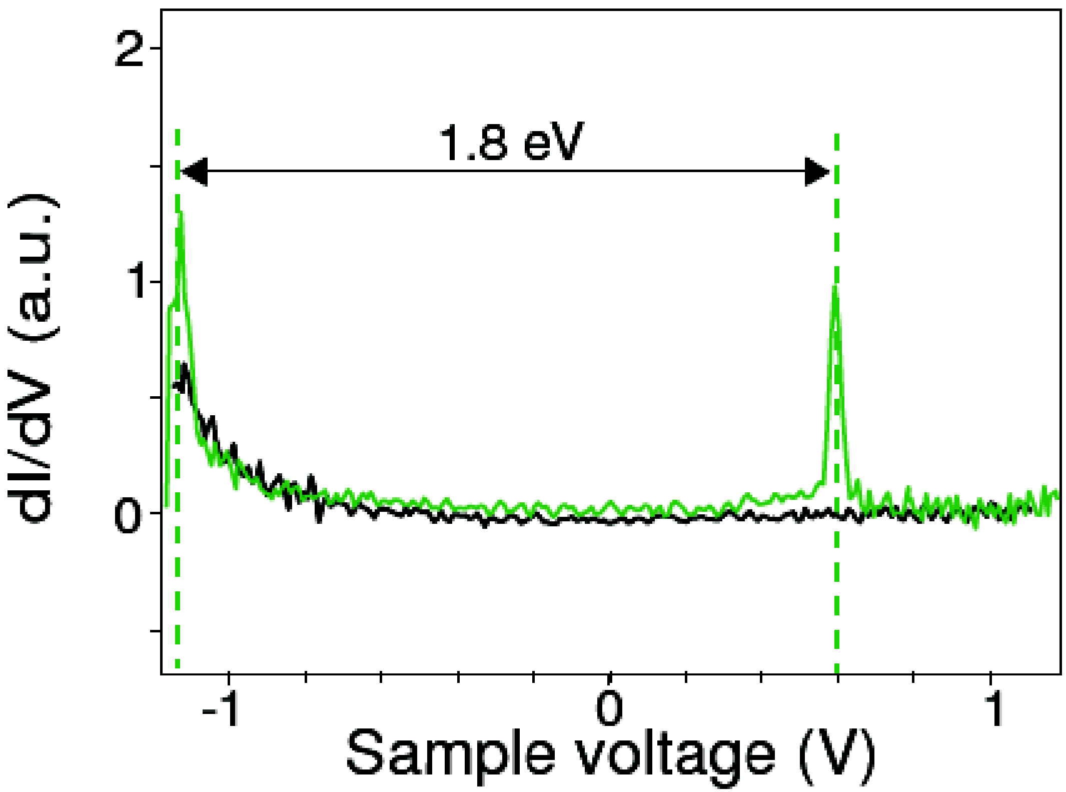
Presence of the NV^{-1} electronic states



Presence of the NV^{-1} electronic states



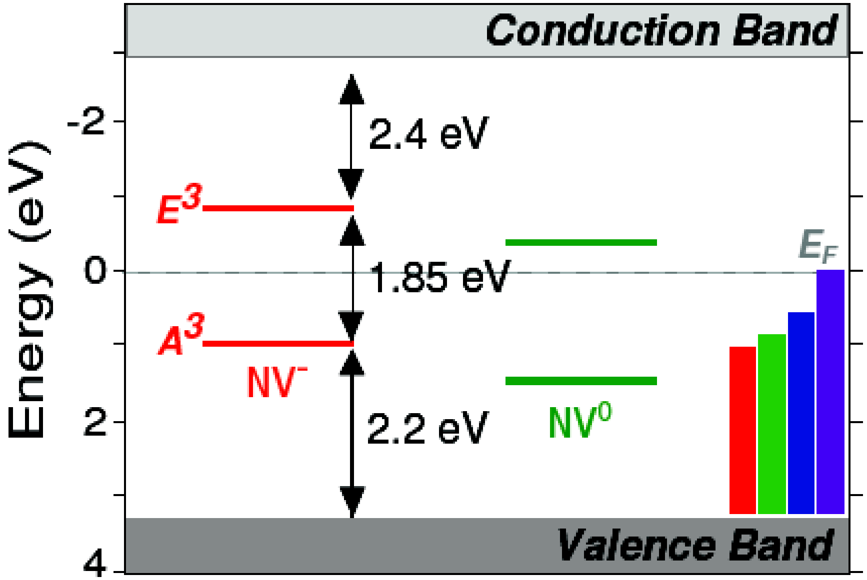
Presence of the NV^{-1} electronic states



- ***HOMO-LUMO states of NV^{-1}*** appears within the ND band gap under illumination

- HOMO-LUMO gap = 1.8 eV

- NV^{-1} transition :
Calculation (1.75-1.8eV)
Experiment (1 .8-1.9eV)



Applications

Promising DNPs applications

Biomedical (drug delivery, fluorescence imaging) [1,2]
Sensors (MEMS sensing, SAW sensing) [3,4]
Color centers (spintronics, single photon sources) [5]
Other (thermal [6], neutron physics [7], …)

Crucial properties and challenges:
state of surface (chemical, structural, electronic)

Need of sensitive characterization of individual DNP on surfaces
Surface potentials related to surface termination and applications
KPFM – proven to be sensitive and effective on bulk diamond

[1] Nanodiamonds: Applications in Biology and Nanoscale Medicine, edited by Dean Ho, Springer **2009**

[2] T. Takimoto et al. Chem. Mater. 22, **2010,** 3462-3471

[3] R. K. Ahmad et al. Appl. Phys. Lett. 97, **2010,** 093103

[4] E. Chevallier et al. Sensors and Actuators B 154, **2011**, 238-244

[5] Y. Chang et al. Nature Nanotechnology 3, **2008**, 284-288

[6] M. Abyzov et al. J. Mater. Sci. 46, **2011**, 1424-1438

[7] V. Nesvizhevsky et al. Materials 3, **2010**, 1768-1781

Drug delivery