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Surface and bulk defects of diamond and correlated electronic variations

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Outline:

I. Surface Properties

- Morphology
- Termination
- Surface Band Bending
- Schottky Contact Properties

II. Bulk properties

- Mobilities
- P1 and H1 Centers
- $\mu\tau$-Products
- Deep Defects

Acknowledgement

- Dr. Zeisel (ODLTS) — WSI, Germany
- Dr. Rezek (AFM) — AIST, Japan
- Dr. Yang (electrochemistry) — AIST, Japan
- Dr. Takeuchi (TPYS) — AIST, Japan
- Dr. Ri (wet chemical etching) — NIMS, Japan
- Dr. Tokuda (homo-epi growth) — AIST, Japan
- Dr. Watanabe (homo-epi. growth) — AIST, Japan
- Dr. Misouchi (EPR) — Univ. Tsukuba, Japan
- Dr. Gräff (EPR) — Uni. Sao Paulo, Brasil

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I.a) Surface Morphologies

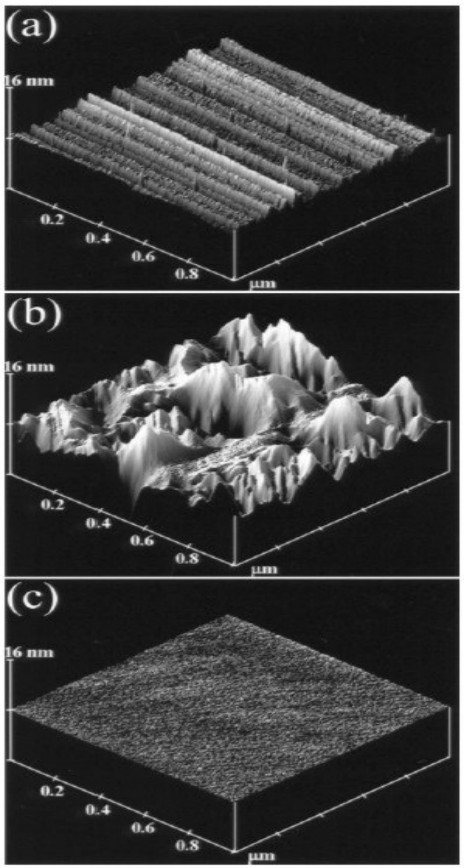
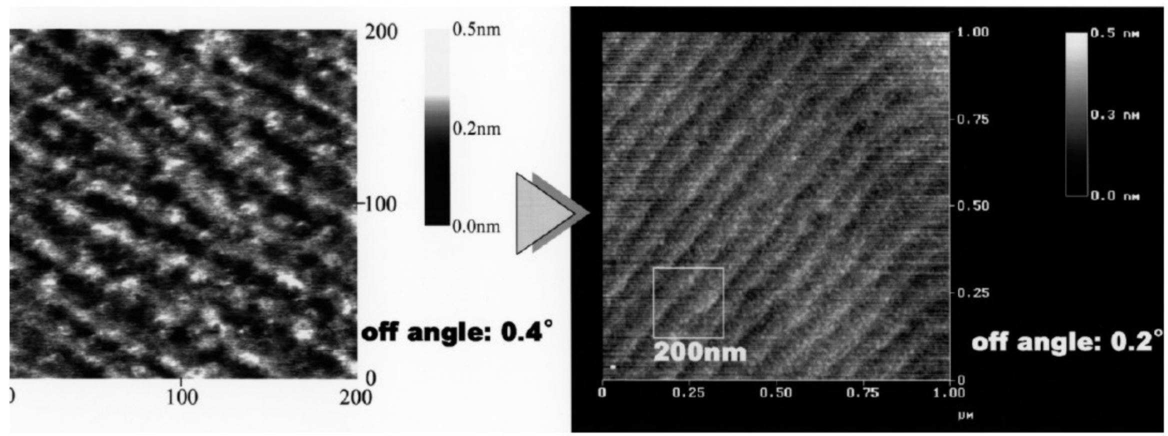


Fig. 3. AFM top view images of (a) surface of as-received Ib (001) substrate, (b) surface treated by the H-plasma (i.e. 0% CH_4 concentration) for 6 h, and (c) growth surface at 0.025% CH_4 concentration for 42 h.



2. Typical surface morphologies of the homoepitaxial diamond film in region III in Fig. 1. (a) a top-view AFM image (200 nm × 200 nm × 0.5 the surface morphology for the misorientation angle of 0.4° at 0.025% CH_4/H_2 ratio for 42 h deposition, and (b) a top-view AFM image (1 × 1 µm × 0.5 nm) for the misorientation angle of 0.2° at 0.025% CH_4/H_2 ratio for 6 h deposition.

Atomically flat surface with step-etch growth.
Terraces run parallel to the (110) direction

H.Okushi, Diam. Rel. Mat. 10, 281 (2001)

Homo-Epitaxial Growth of CVD Diamond (AIST)

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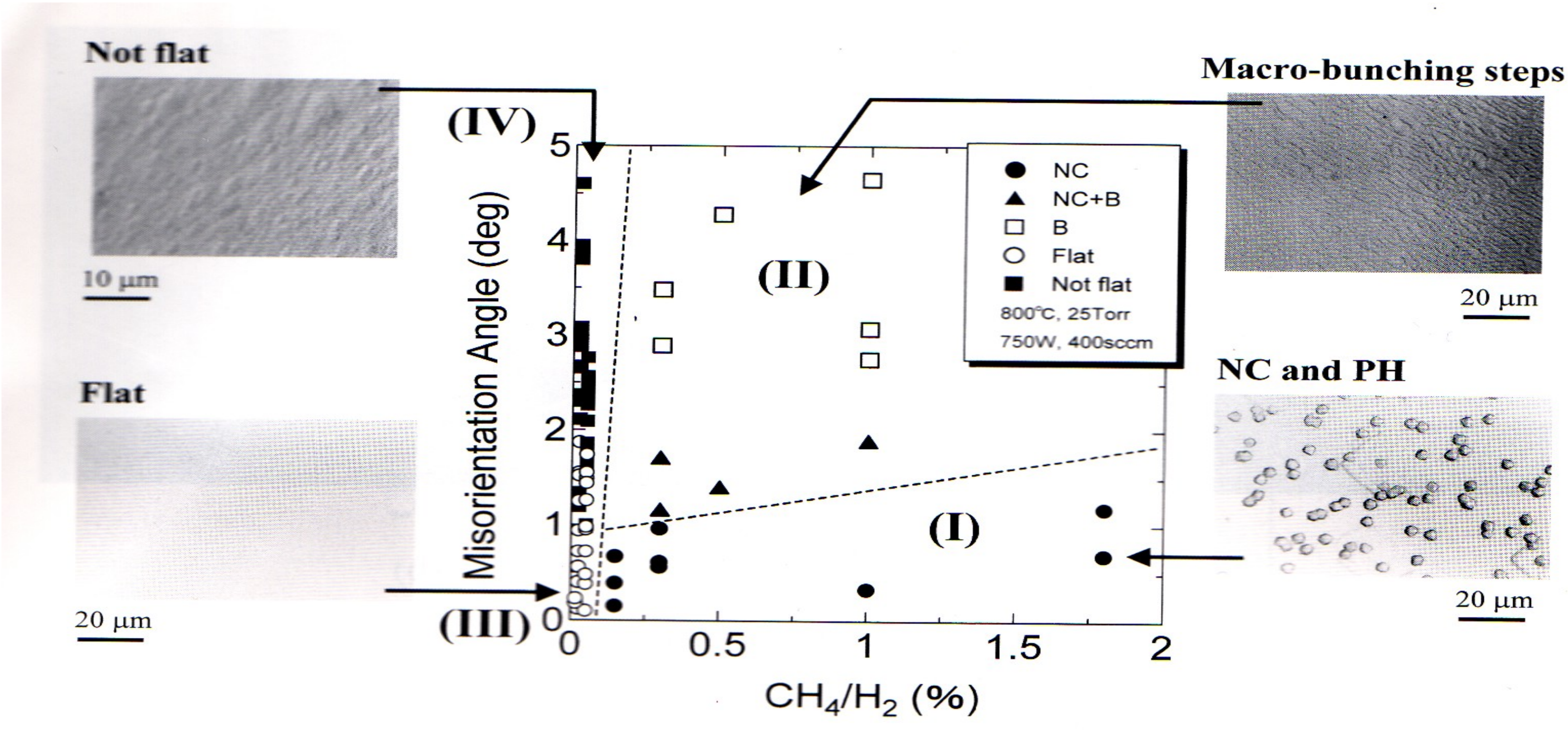


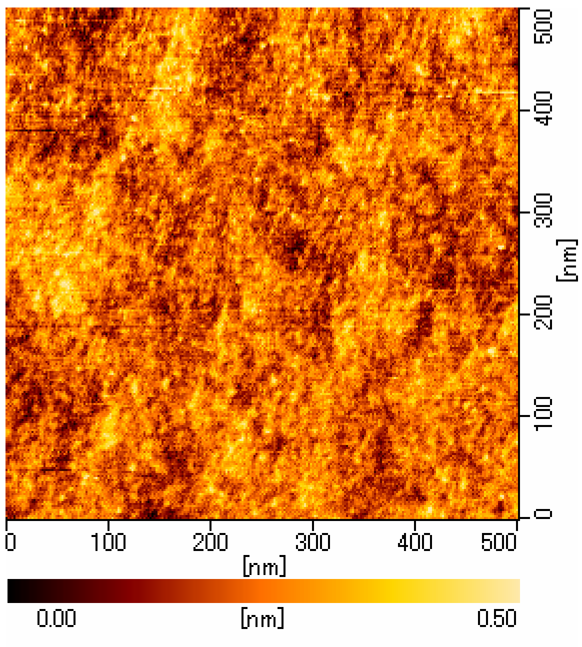
Fig. 1. Map of the surface morphology as a function of both the misorientation angle and the CH_4/H_2 ratio.(1) The dotted lines in the figure serve as a guide to the eye and are used to divide the area into four regions I–IV. A detailed explanation is given in the text.

H. Watanabe et al., New Diamond and Frontier Carbon Technology, 12, 369 (2002)

but: extremly low growth rate (10 nm/h)

Surface Properties of Homo-Epi. Diamond

“Atomically” Smooth Surface
RMS = 0.8 Å



“Truly Atomically” Smooth CVD Diamond

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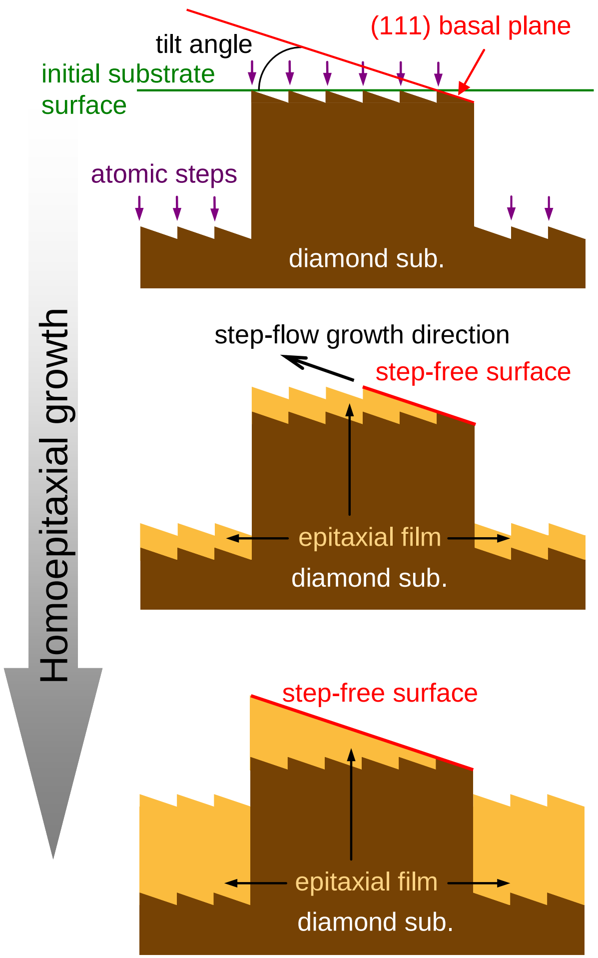
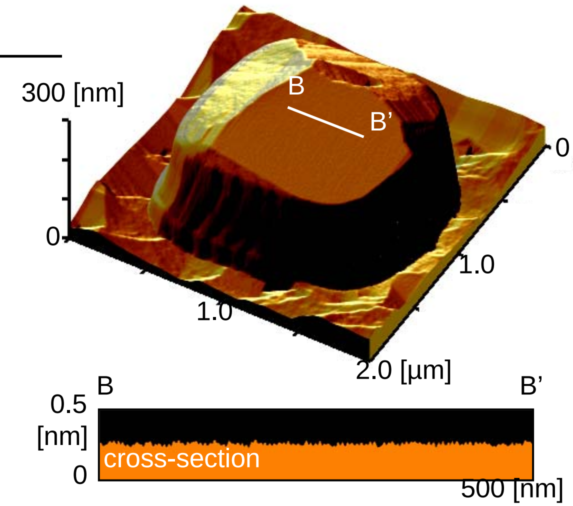
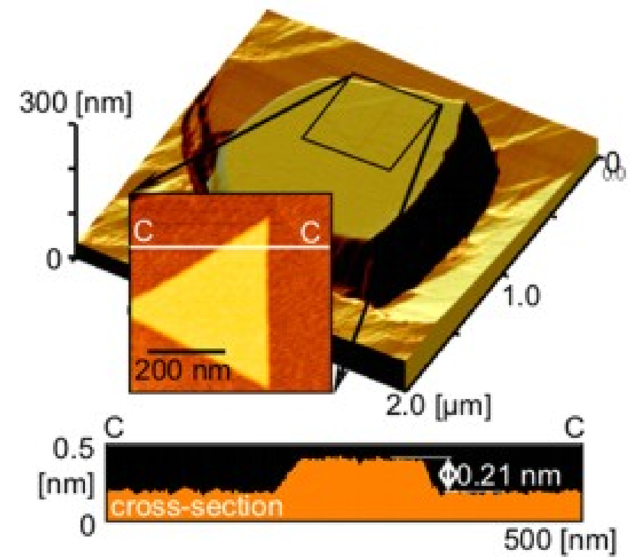
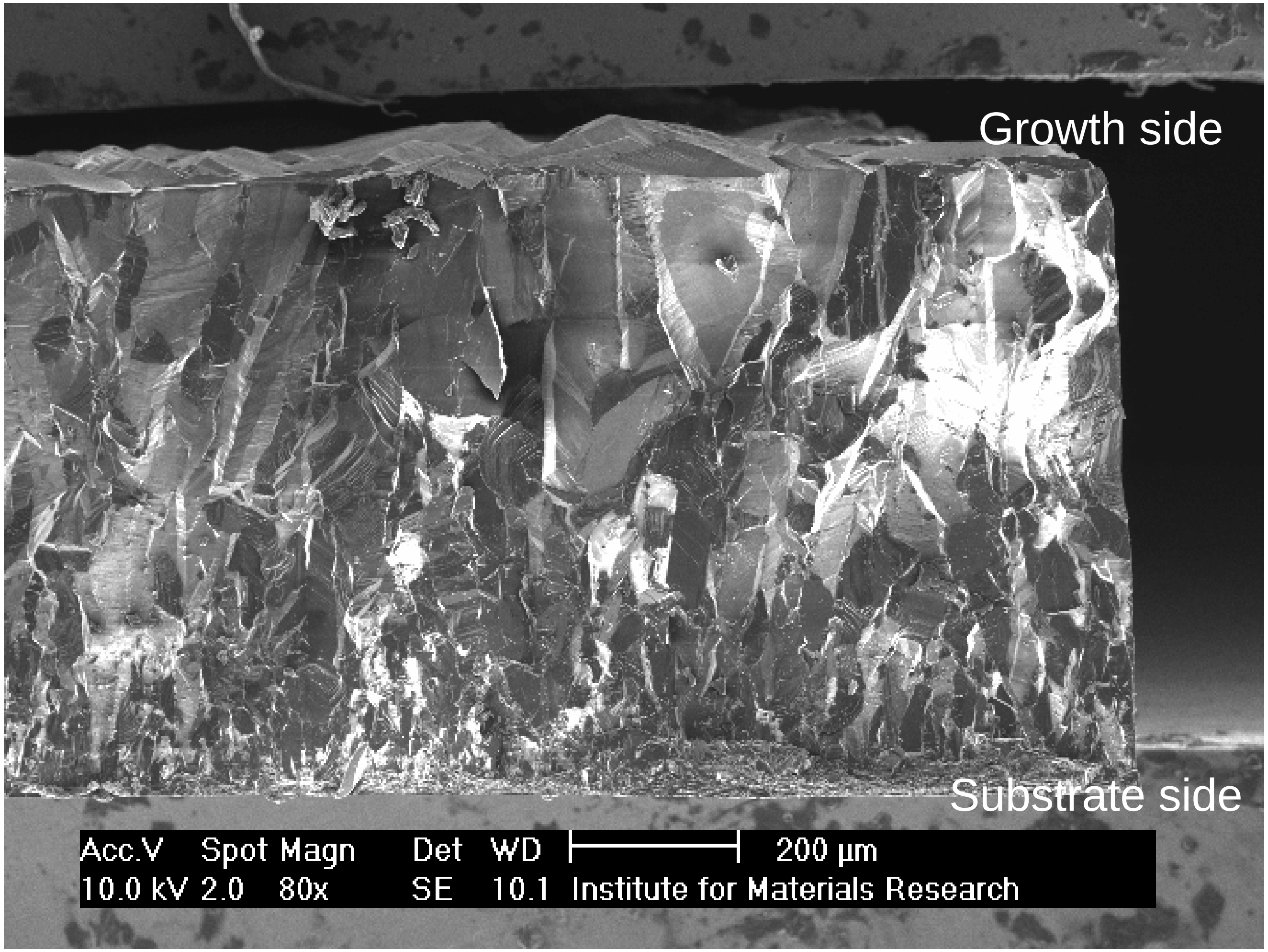
N. Tokuda et al. sub.







Polycrystalline CVD Diamond:



fast growth, large area

M. Nesladek

Fraunhofer
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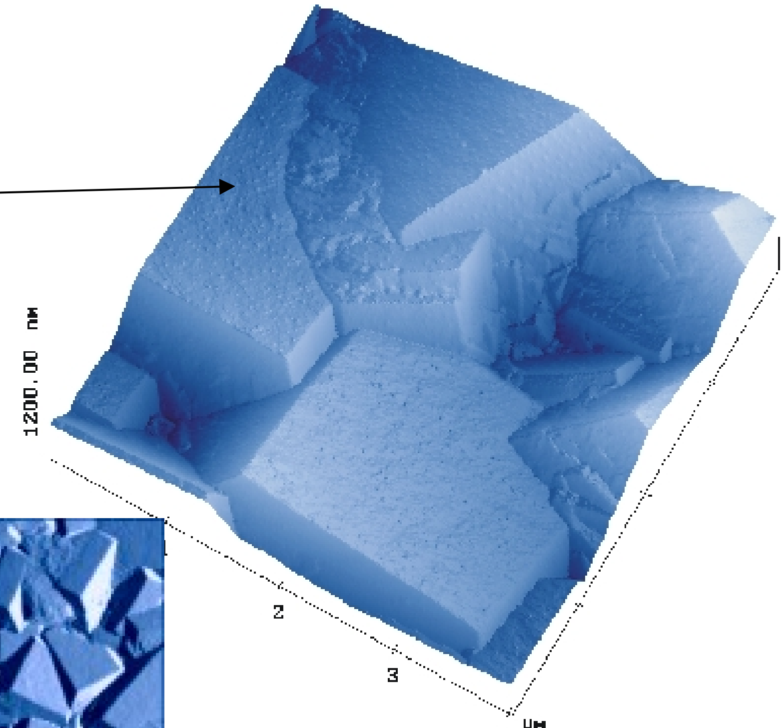
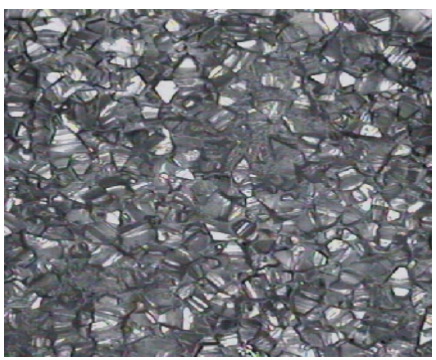
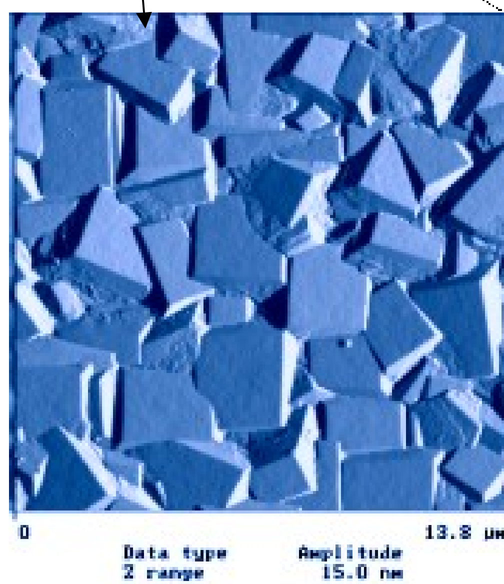
Diamond Surface: Poly CVD Diamond

Crystallite roughness about: 20 – 50 μm

Roughness on planes: 10 – 20 nm



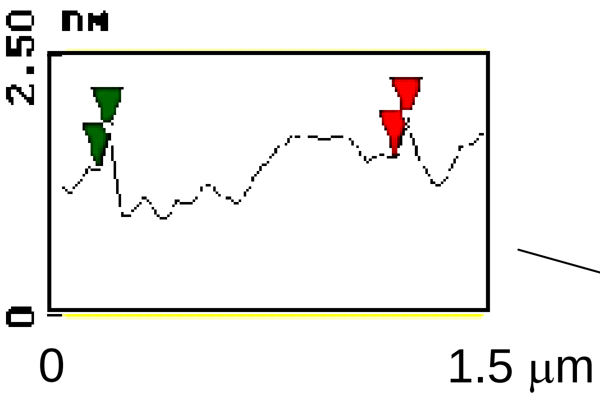


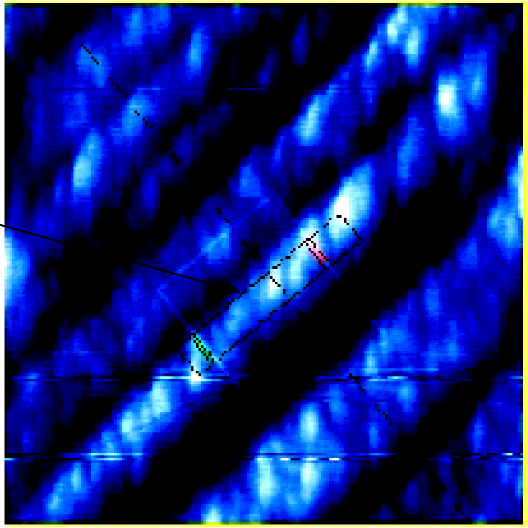


Polished Diamond

Polishing Roughness: 2 - 15 nm

Fine structure roughness: 5 A





I.b) Diamond Surface Terminations C(100)(2x1)

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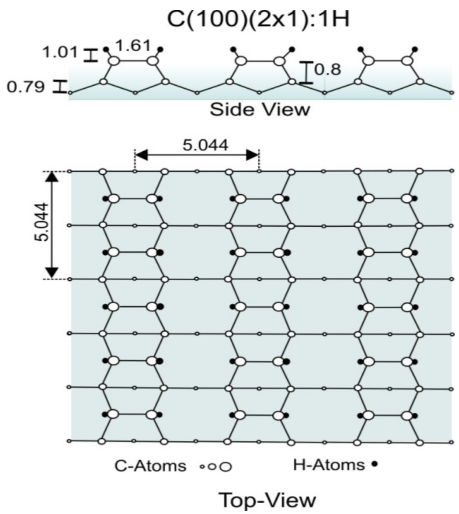
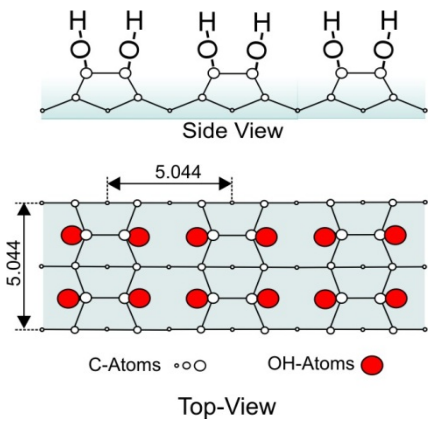
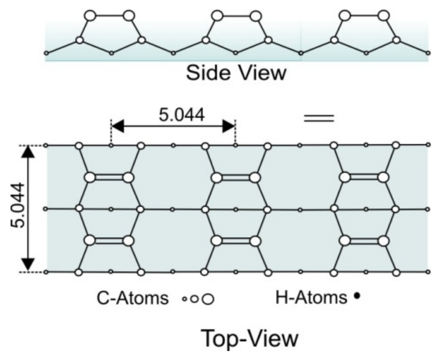
Hydrogen Terminated Diamond



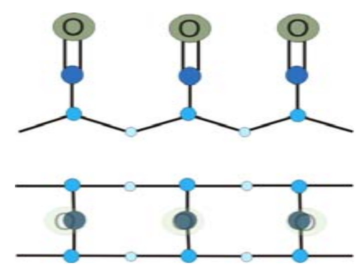
Wet-chemically or electrochemically oxidized



Reconstructed Diamond

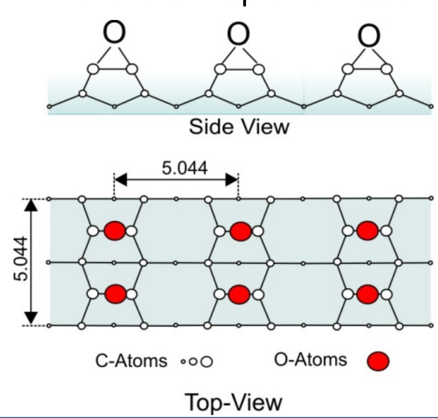


Plasma-oxidized Diamond

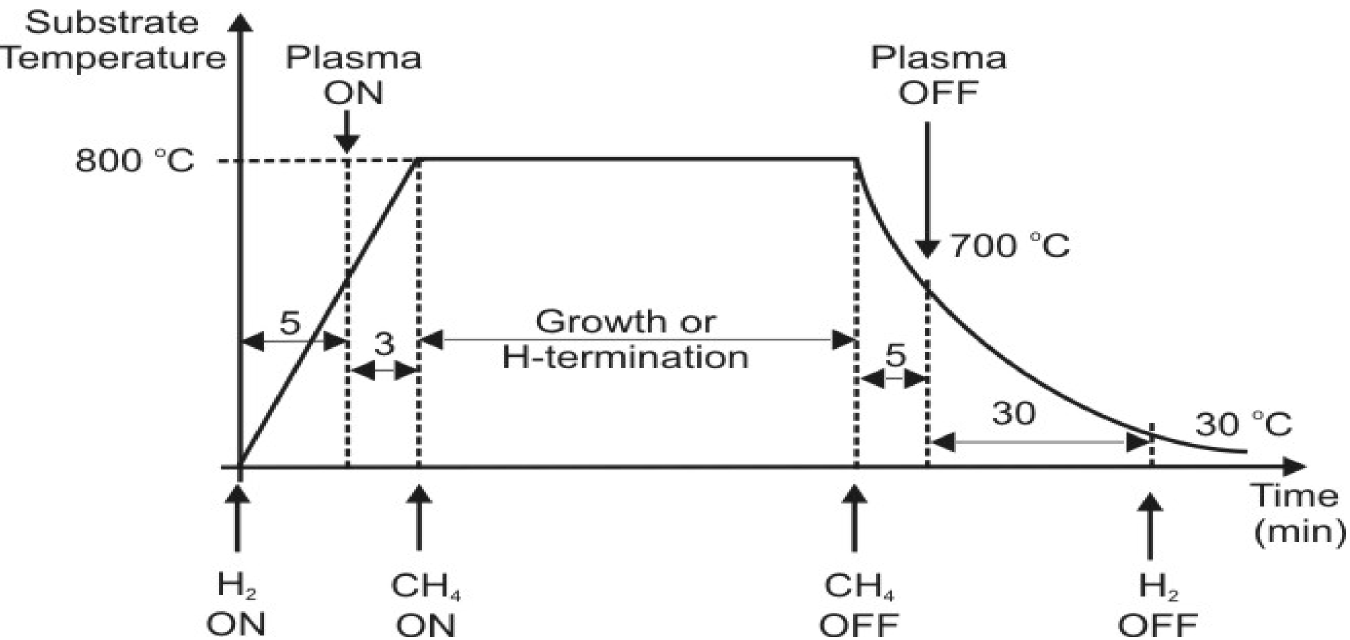


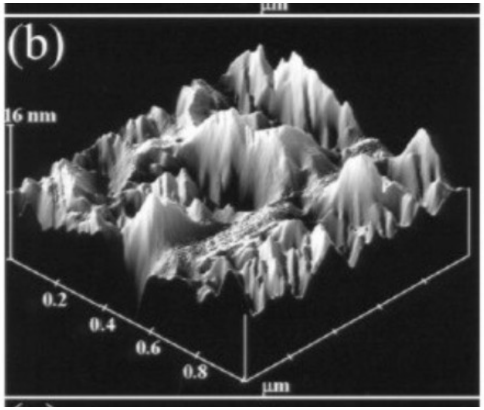
Ether or Bridge Site Model

Ketone or Top Site Model



H-Termination





after 6 h H-plasma

H-termination parameter

sample		**d01**
date		*8.6.04*
stage temperature	[°C]	800
microwave power	[W]	750
total gas pressure	[Torr]	25
total H2 flow	[sccm]	400
total CH4 flow	[sccm]	0
exposure time	[min]	5
plasma off at	[°C]	700

Defect Free: C(100)-(2x1):H

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H-termination: ex-situ at 800 °C, for 1h

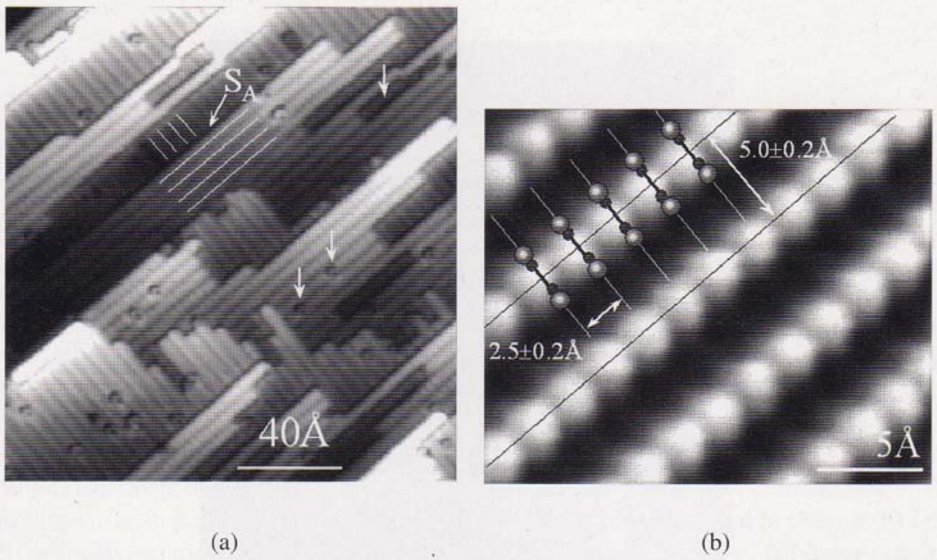
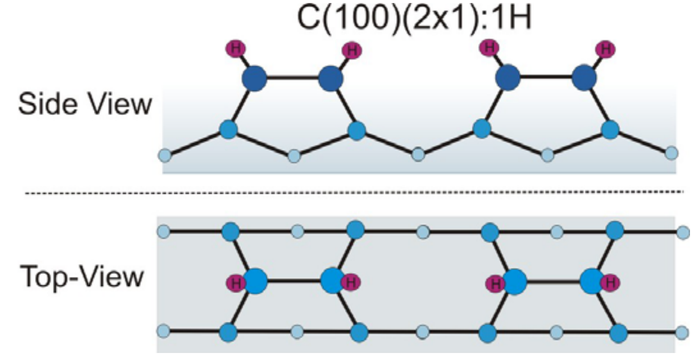


Fig. 2. STM topographies of the hydrogenated diamond C(100)-(2×1):H surface: (a) $U_{bias} = +1.5$ V, $I_t = 1.5$ nA (unoccupied states) and (b) $U_{bias} = -1.5$ V, $I_t = 1.0$ nA (occupied states). The bright lines on the top topography indicate the C-C dimer rows in the vicinity of the step (S_A). Reproduced from ref. 9.



- Microwave Plasma CVD
- Hot Filament Technique

"Atomically" flat surface with mono-atomic steps

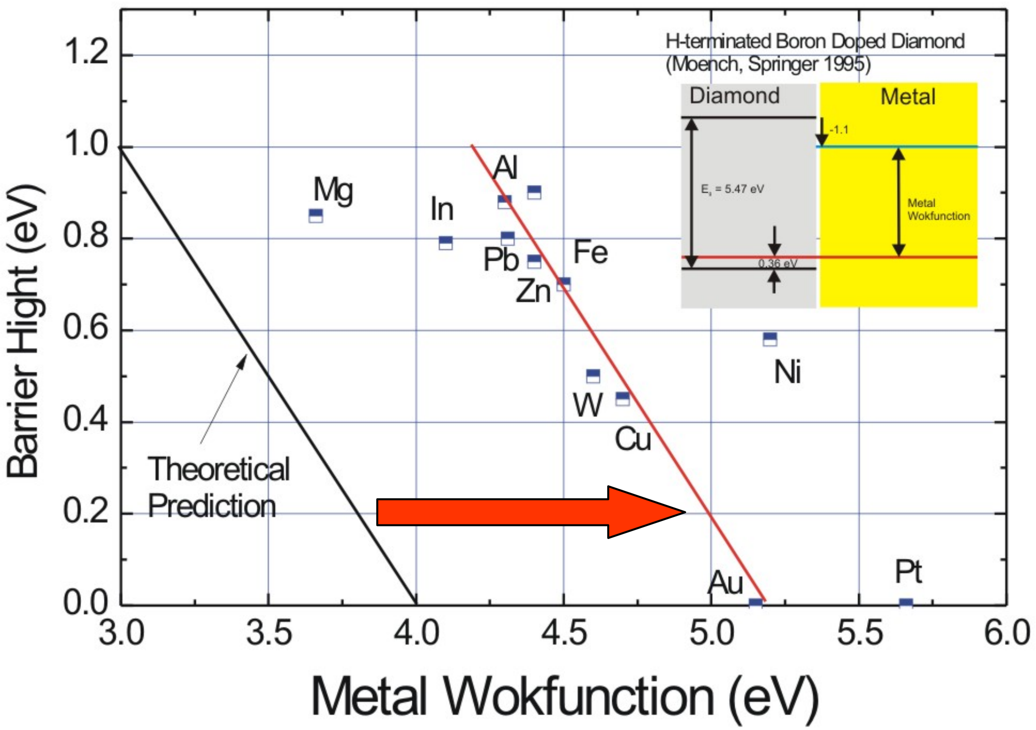
A. Maynev, G. Dujardin, New Diamond and Frontier Carbon Technology 15 (2005) p. 265.

Summary H-termination

- **<u>If H-termination is optimized:</u>**
- Unpinned Surface Fermi level
- High quality surface with minimized defect density
- Schottky-Mott Law ok ?

<u>Schottky Barrier Hight:</u>

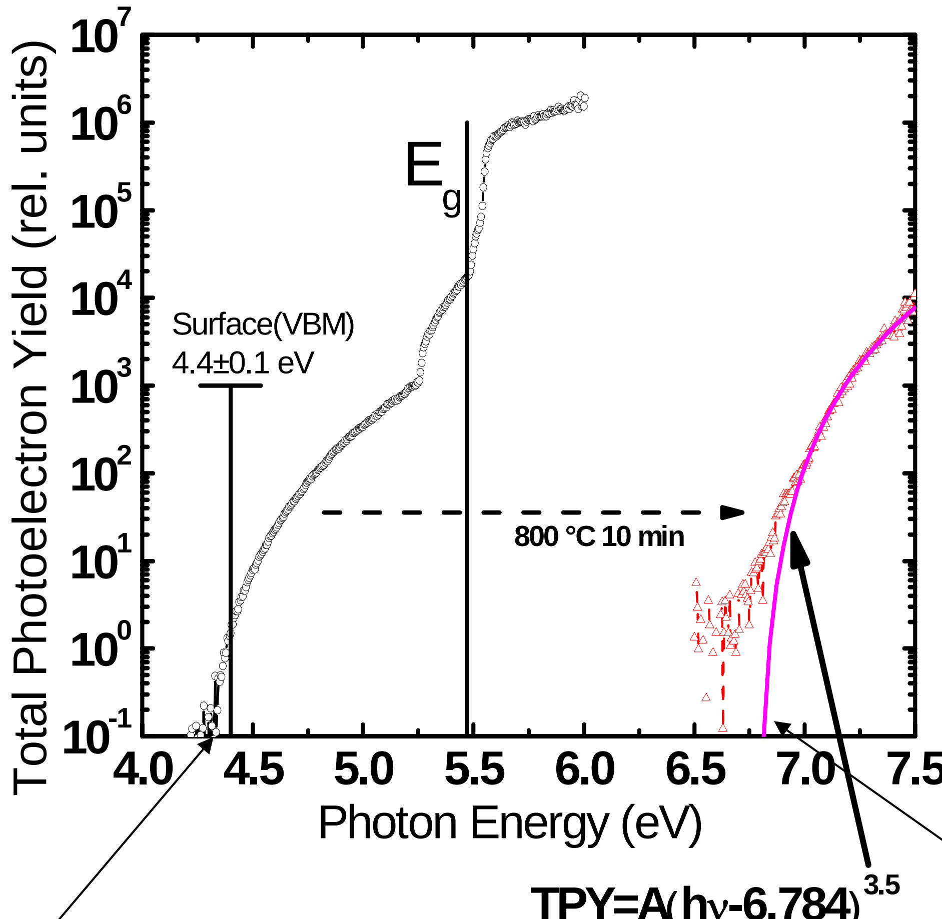
$$q\Phi_{Bn} = q(\Phi_m - \chi)$$



<u>But:</u>

- Data in literature does not show NEA properties
- 1.2 eV shift

Electronic Surface Properties



Maier, Ley, Ristein et al.

Takeuchi et al.

H-termination:
negative electron affinity: -1.1 eV

UHV annealed sample (800 °C):
positive electron affinity: +1.2 eV

Band Bending of H-Terminated Diamond

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$$Q_{sc} = qN_D W = \sqrt{2q\epsilon_s N_D(V_{bi} - V)} \qquad \text{C/cm}^2$$

$$C = \left|\frac{\partial Q_{sc}}{\partial V}\right| = A\sqrt{\frac{q\epsilon_s N_D}{2(V_{bi} - V)}} = \frac{\epsilon_s}{W} \qquad \text{F/cm}^2 .$$

Equation 10 can be written in the form

$$\frac{1}{C^2} = \frac{2(V_{bi} - V)}{A^2 q\epsilon_s N_D}$$

Built-in Potential V_{bi}
Acceptor Density N_D

or

Doping Profiling as function of x:

$$\frac{-d(1/C^2)}{dV} = \frac{2}{q\epsilon_s N_D A^2}$$

$$N_D = \frac{2}{q\epsilon_s A^2}\left[\frac{-1}{d(1/C^2)/dV}\right].$$

$C=\varepsilon_o\varepsilon_r A/w$

Gives Depth

Gives Acceptor Density

H-term. Boron doped Diamond in 1 M H_2SO_4

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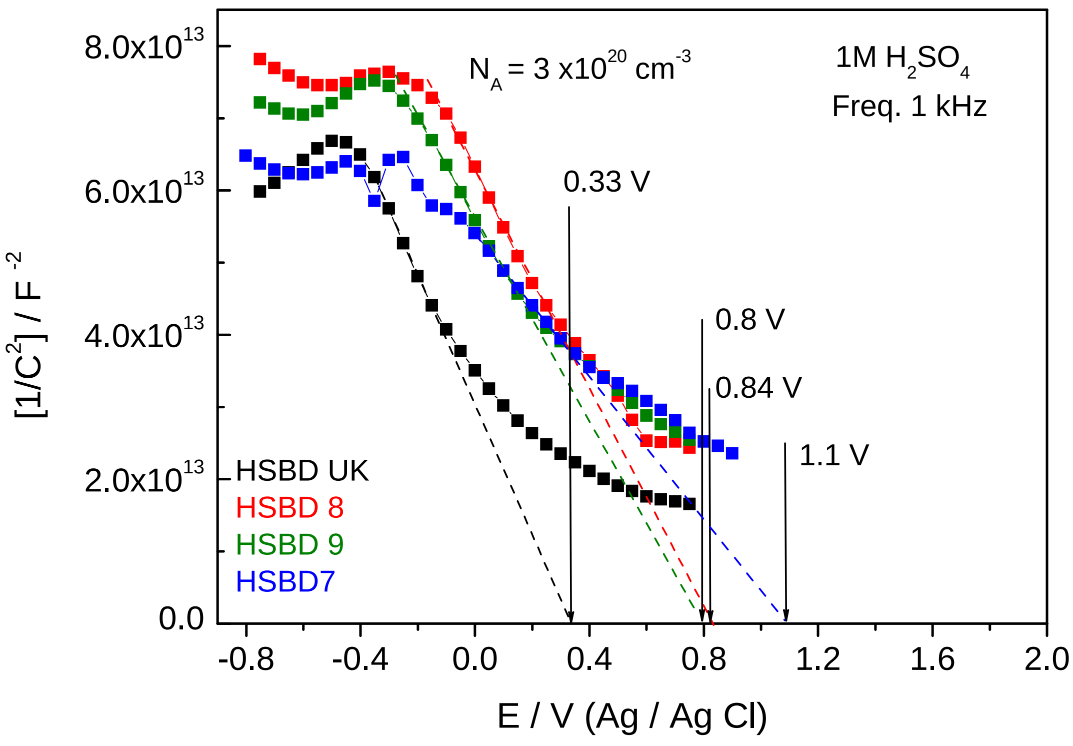
Capacitance Voltage Spectroscopy



Built-In Potential: 0.3 – 1.1 V

Energy Barrier: 0.66 – 1.46 eV

Capacitance of Depletion Layer: 5 µF/cm^2

Diamond Interface To Buffer

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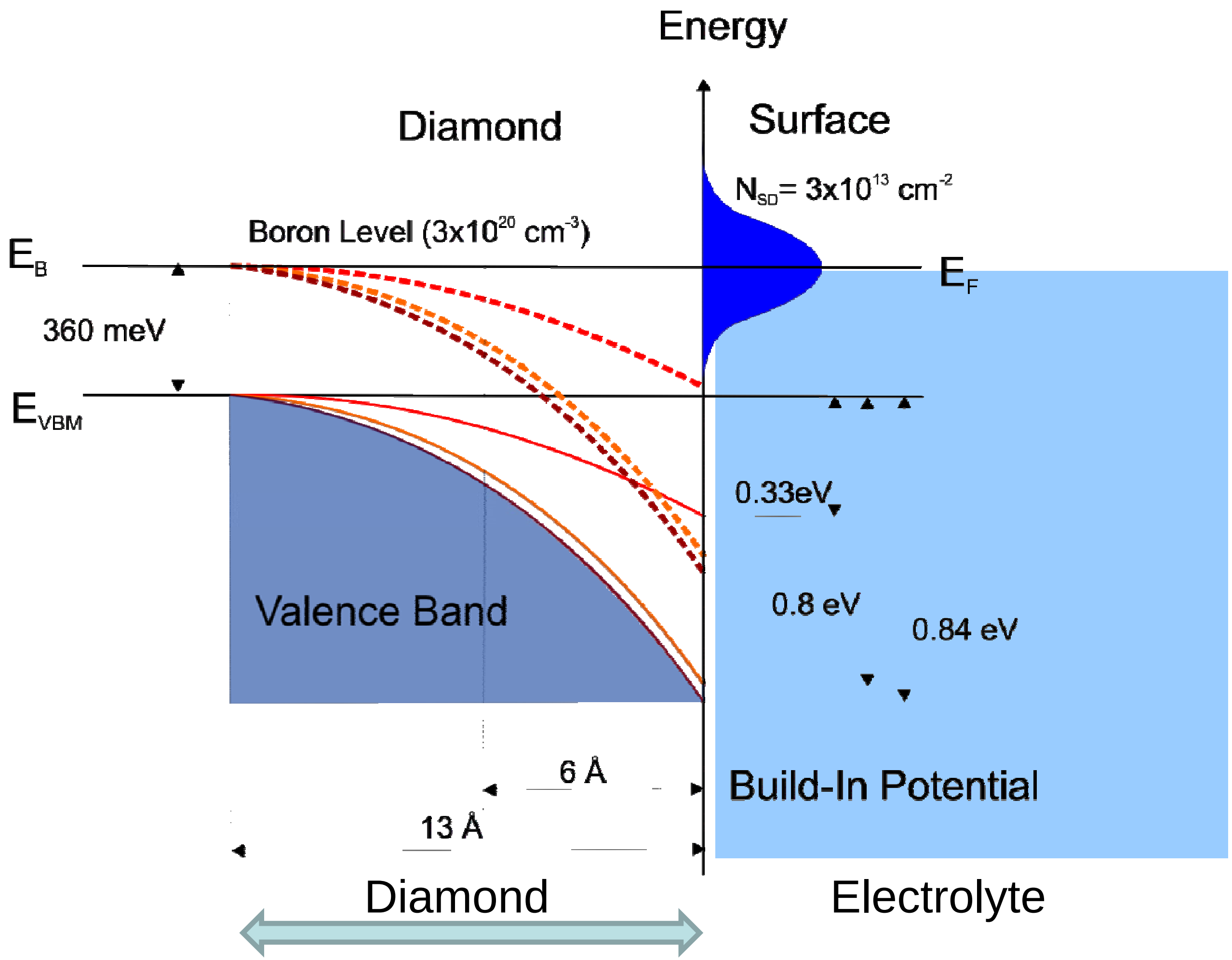


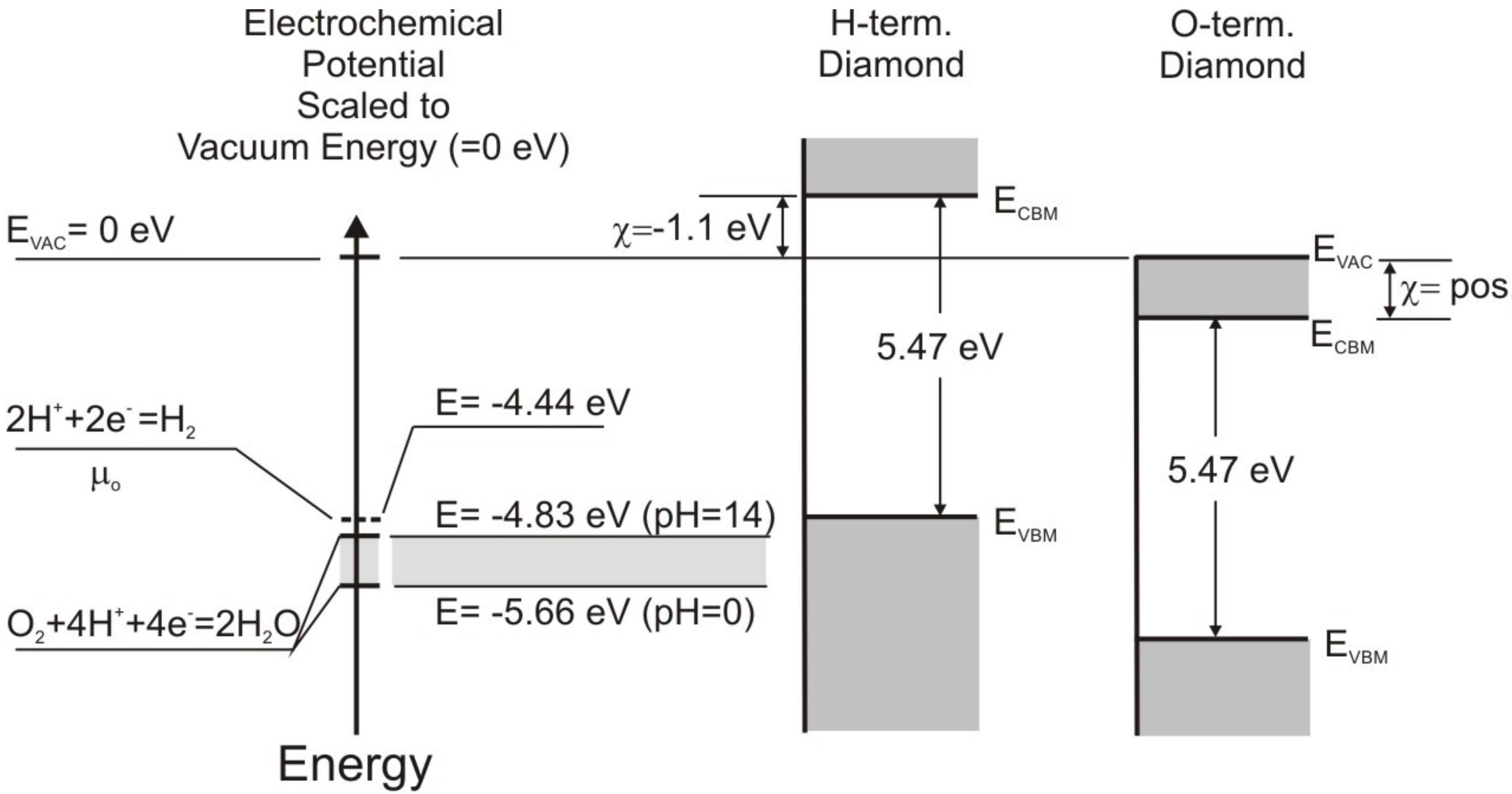
Capacitive Layer Width: 10 Å
Small Capacitance !

Remember Metals:

Charge separation at interface:
1 to 2 Å
(“Helmholtz Capacitance”):
Large Capacitance !

Background Current: I = v C

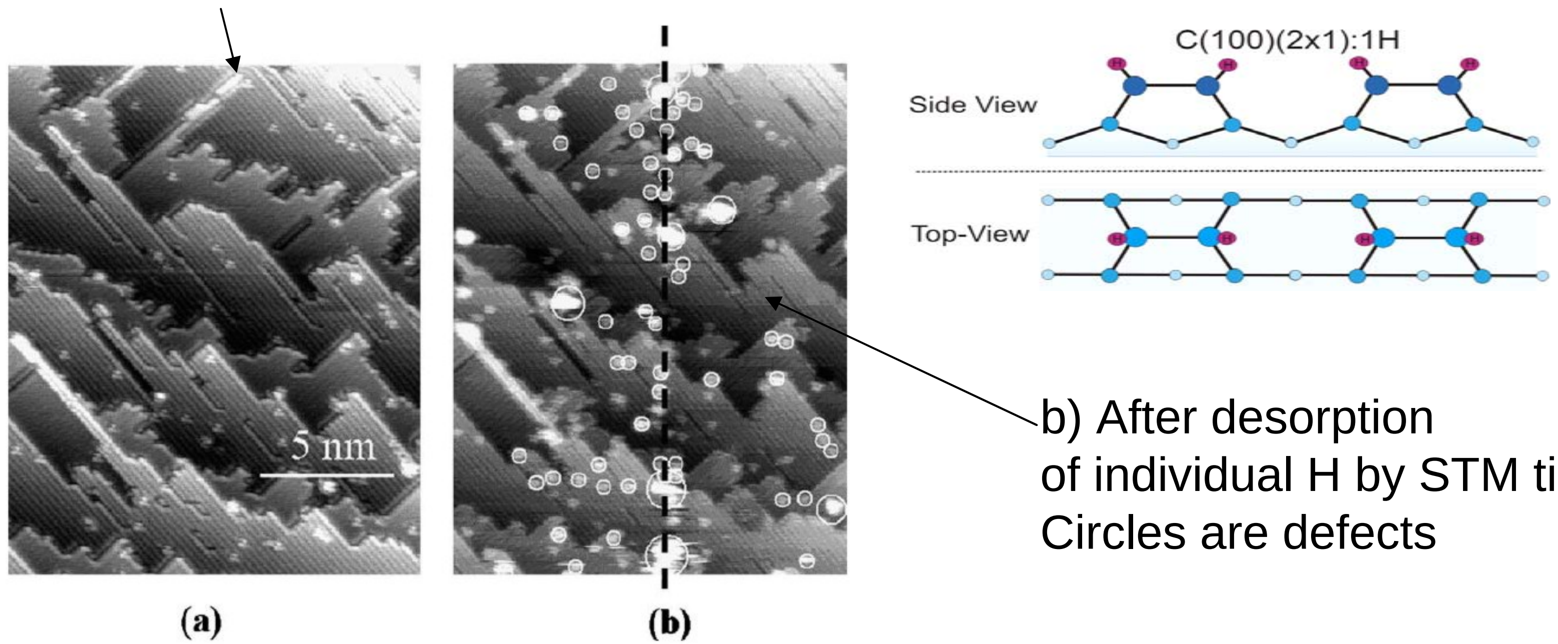
Energy Levels of Buffers



Local Oxidation (STM): C(100)-(2x1):H

H-termination: ex-situ at 800 °C, for 1h

a): Atomically flat surface with mono-atomic steps



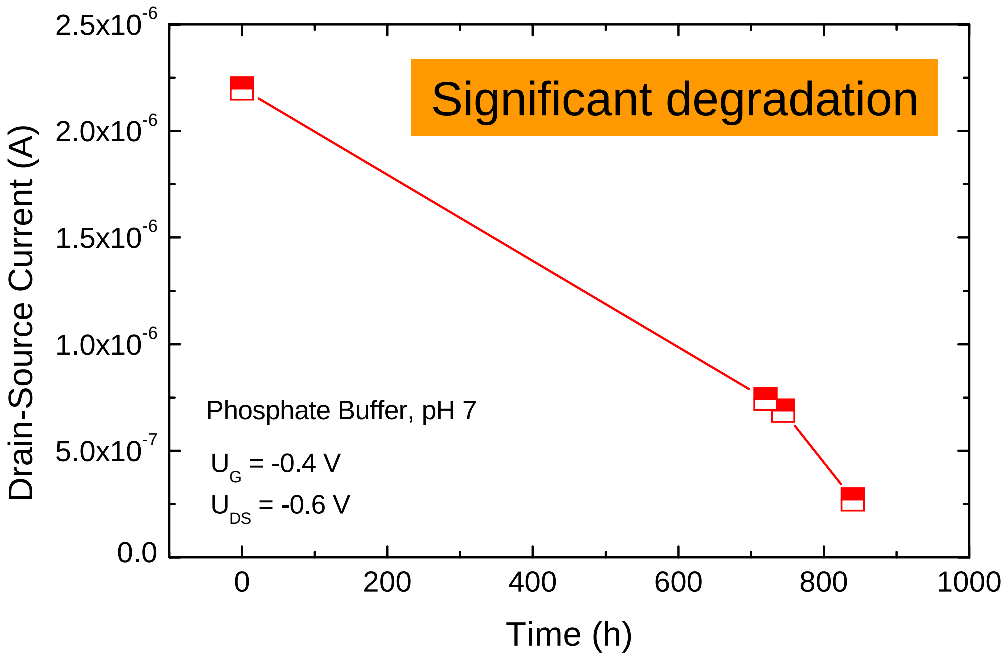
b) After desorption of individual H by STM tip. Circles are defects

Fig. 1. Desorption of hydrogen from the hydrogenated diamond C(100)-(2 × 1):H surface. The corresponding STM topographies (15 × 19 nm) before (a) and after (b) the desorption procedure were recorded at $U_{bias} = -1.5$ V, $I_t = 1.0$ nA. The dashed line in (b) indicates the manipulation line. The bright features in (b), scattered around the dashed line and highlighted by enclosing into white circles, represent the dangling bonds after desorption of individual hydrogen atoms.

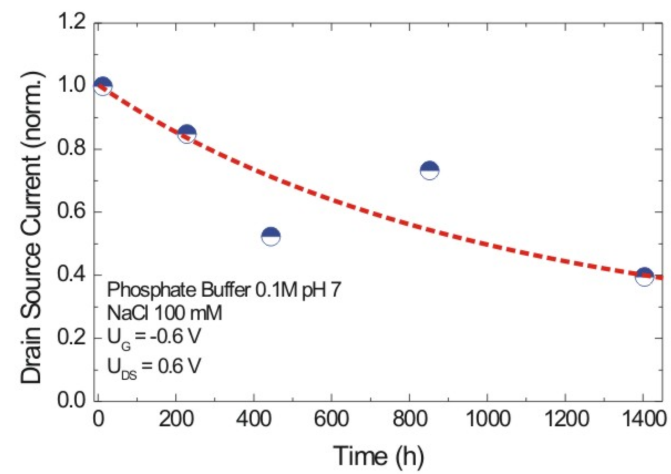
K. Bobrov, G. Dujardin, et al. Surface Science 528, p. 138 (2003)

Surface Degradation

DNA-FET in buffer



FET in Air



Amplitude decrease: 70 % (700 h)

H-term. Surface:
Decrease: 40 % (700 h)

H-terminated diamond in air is chemically not stable

Wet-Chemical/ Electrochemical Oxidation

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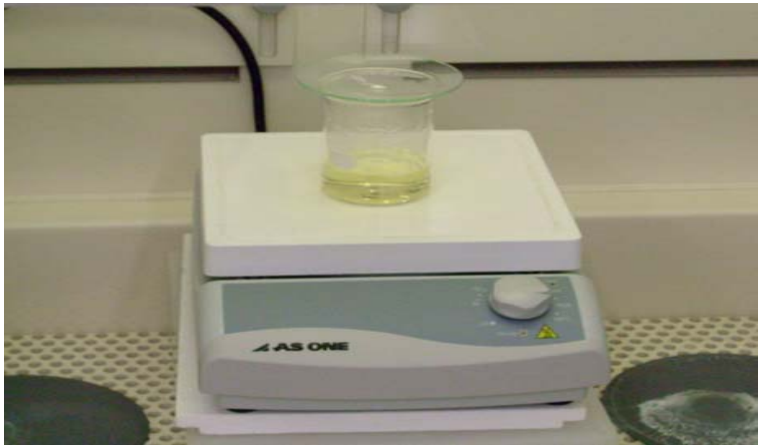
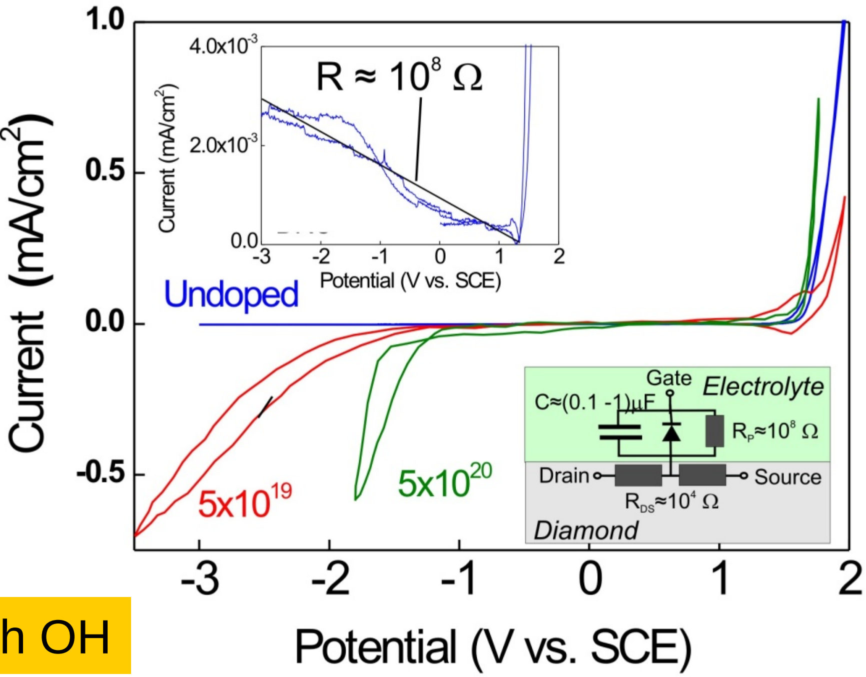


Boiling in:
HNO_3:H_2SO_4 = 1:3
at 230 °C
for 1 h



Termination with OH

but: degree of termination (100 %) ?

H-termination evaluated chemically

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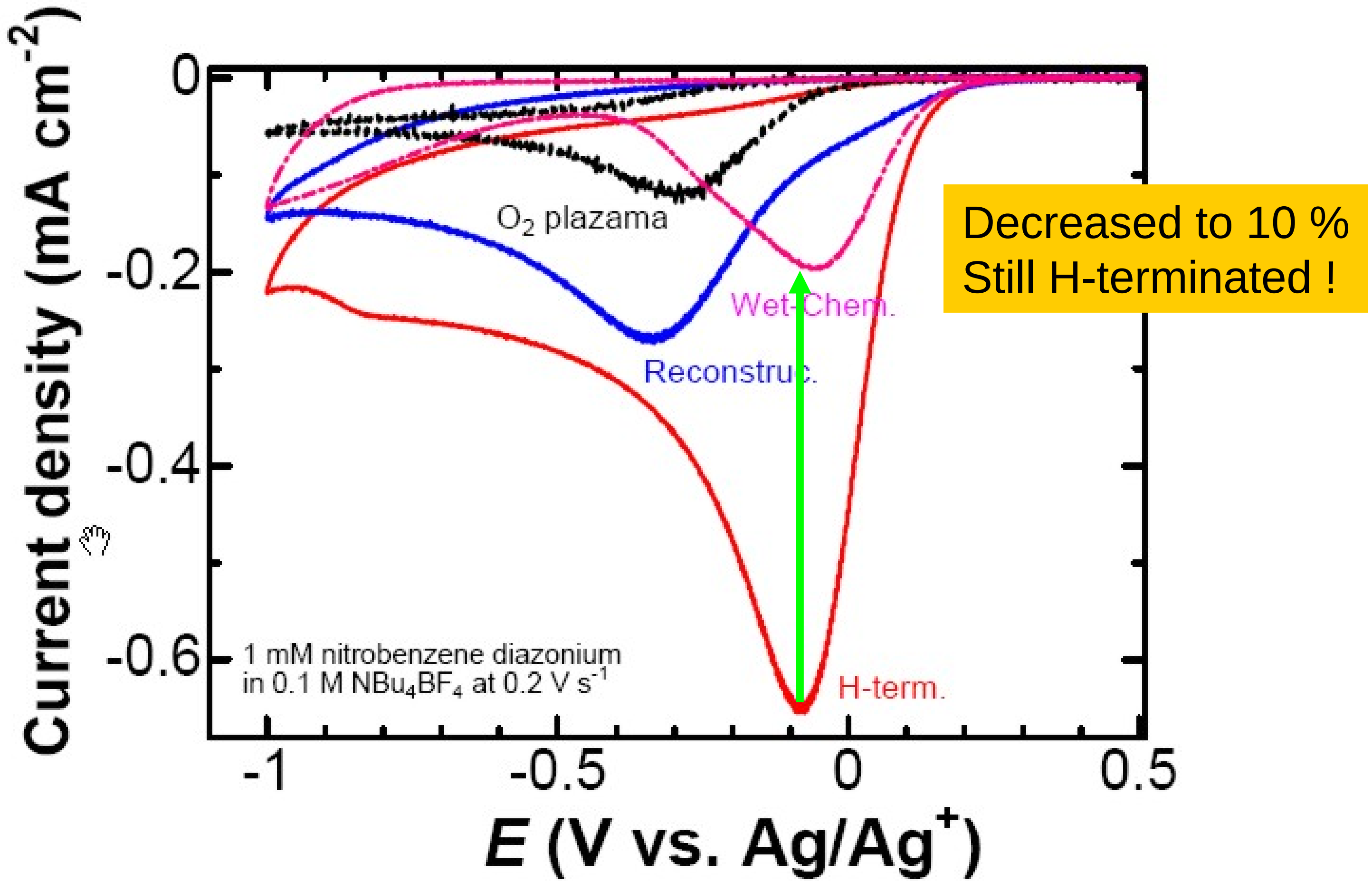

Plasma Oxidation:

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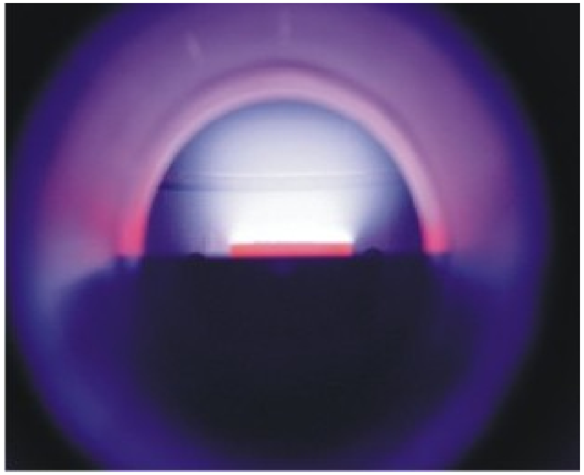
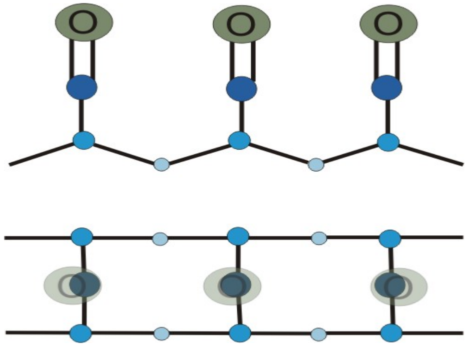


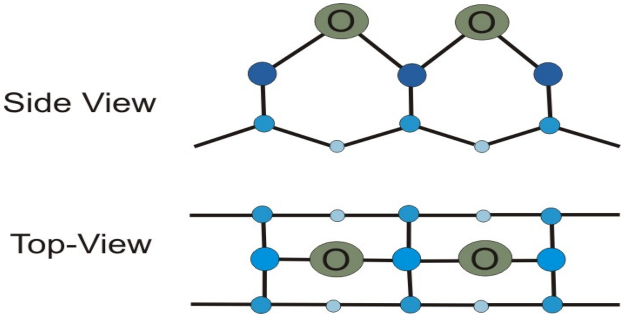
O_2-Plasma:

300 W,
25 Torr,
5 min.

Ketone or Top Site Model



Ether or Bridge Site Model



Reconstruction (ann. 1100 °C)

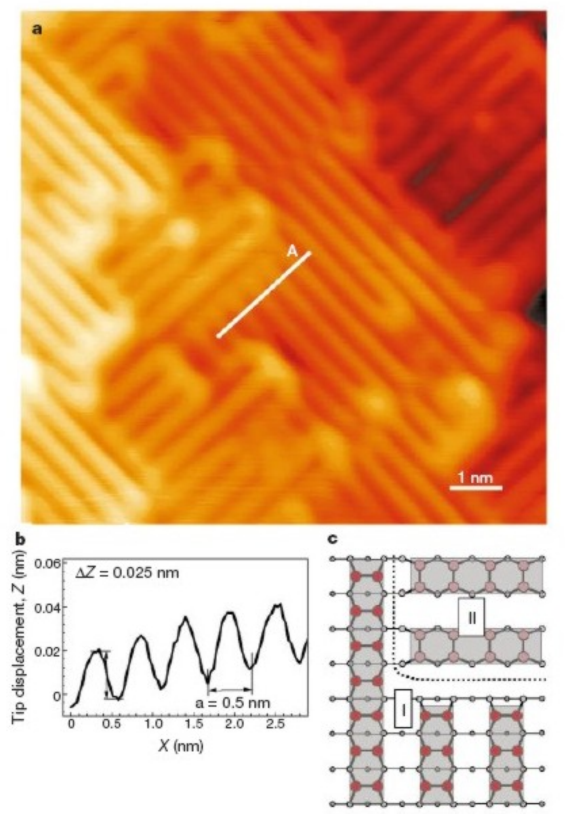
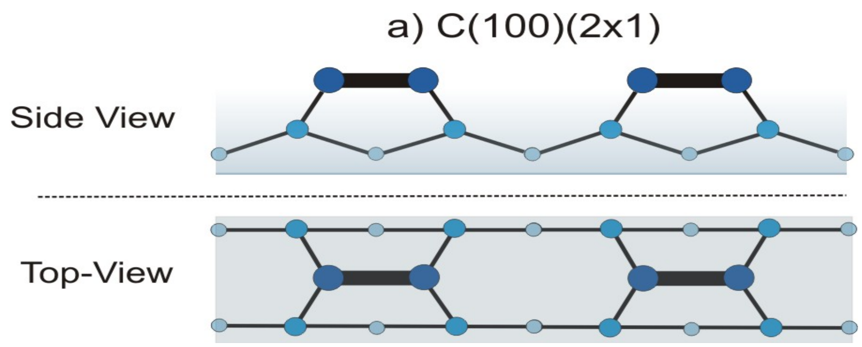


Figure 2 Clean diamond C(100)–(2×1) surface. **a**, The STM topography (10 nm × 10 nm) of the clean diamond surface recorded in the near-field emission regime (U_{bias} = 5.9 V, I = 1.1 nA). **b**, Height variation of the STM tip along the line A. **c**, Top-view of a monoatomic step on the two-domain (2×1) reconstructed surface. The coloured circles represent the carbon atoms belonging to the top four surface layers; the biggest circles represent the carbon–carbon dimers. The domains labelled as I and II represent the upper and lower terrace, respectively. The dimer rows are highlighted by shading, whereas the troughs between them are unfilled. The dashed line shows schematically the boundary between the domains.

H-free surface,
clean diamond

(2x1) reconstruction with
π-bondet dimers



K. Bobrov, G. Dujardin, et al., Nature 413, 616 (2001)

Capacitance/Voltage Evaluation

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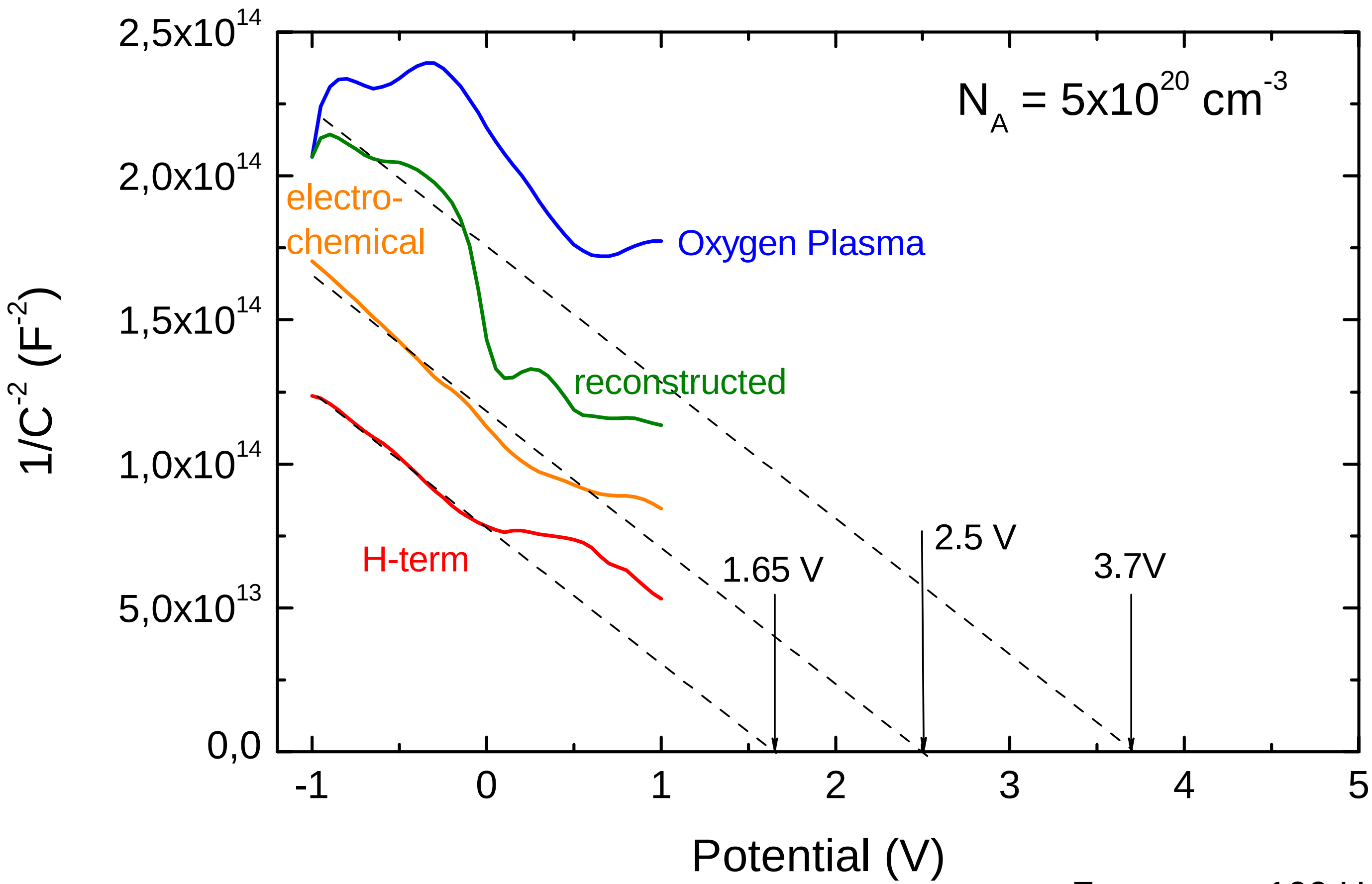

Frequency: 100 Hz

Buffer : Phosphate (no FeCN)

Diamond Interface after Surface Modifications

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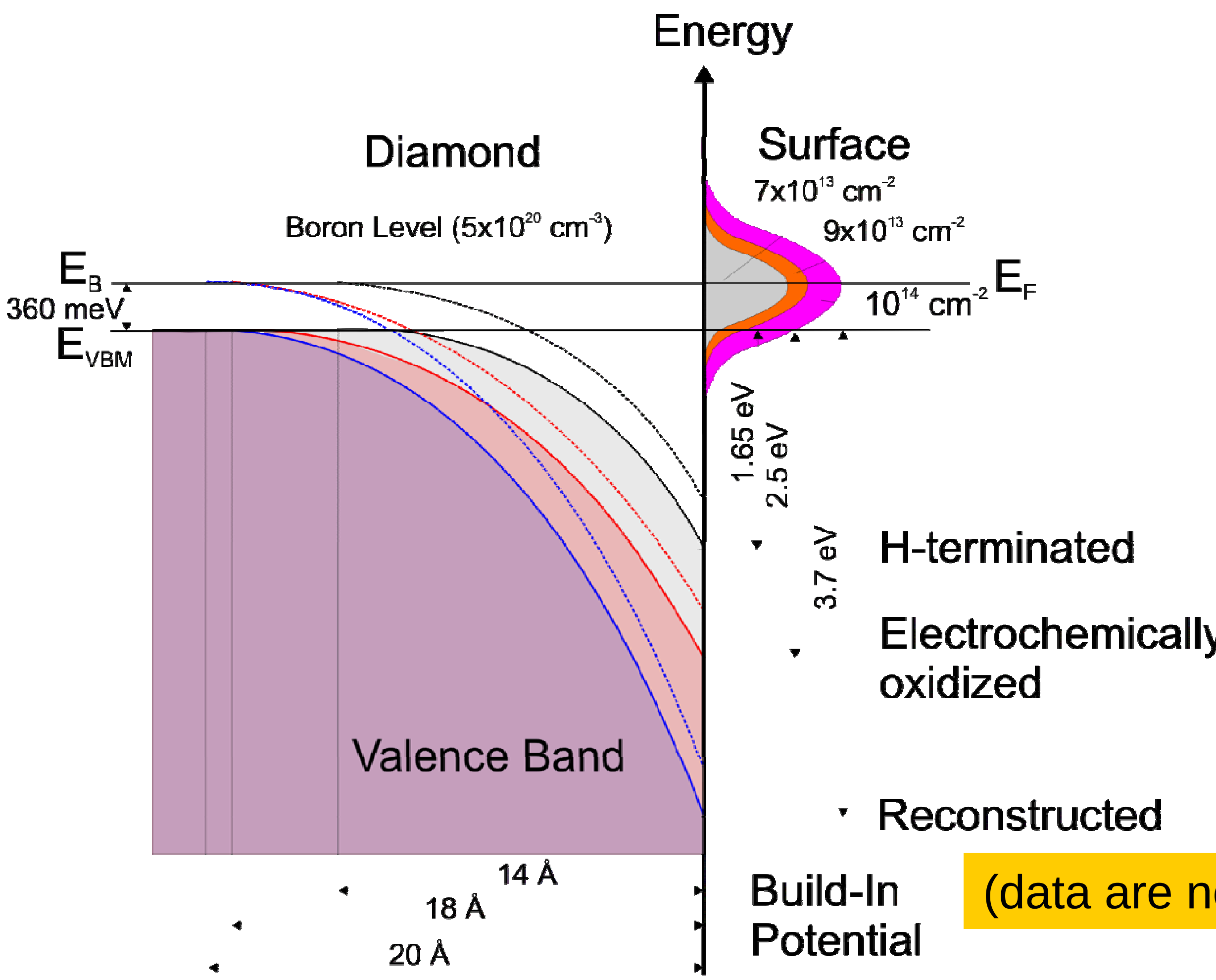

(data are not convincing ?)

Surface Fermi Level (UPS/XPS): $\Delta E = 0.5 – 1.2$ eV

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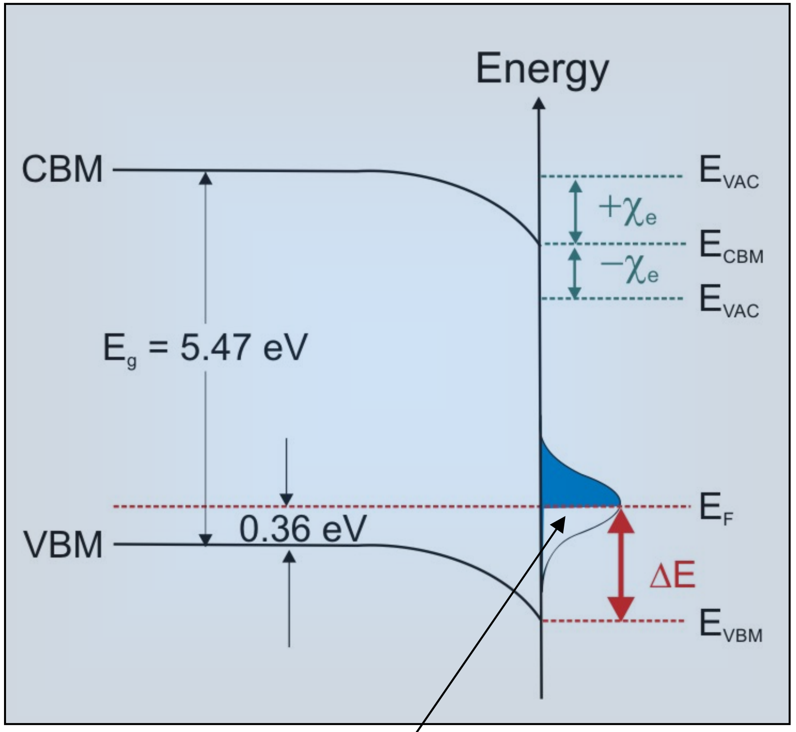
(111)-(2x1) reconstructed: 0.88 above E_{VBM}
J.B. Cui et al. Phys. Rev. Lett. 81 (1998) p. 429.

(100)-(1x1):O 1.2 eV downward bending
Murret et al, Semicond. Sci. Technol. 19 (2004) p. 1.



(100)-(2x1):H 0.3 eV downward Bending
Murret et al, Semicond. Sci. Technol. 19 (2004) p. 1.

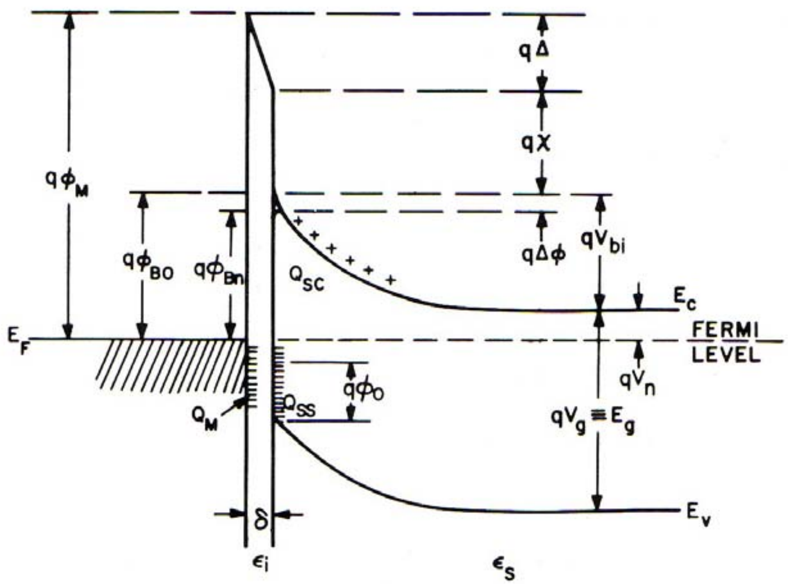
Surface defects

(100)-(2x1):H 0.5 eV above E_{VBM}
Kono et al. Surf. Science 529 (2003) p.180.

Real Schottky Contact

Surface Fermi-level
pinning by
surface defects

Schottky barrier is
not dependent
on metal.



ϕ_M = WORK FUNCTION OF METAL
ϕ_{Bn} = BARRIER HEIGHT OF METAL-SEMICONDUCTOR BARRIER
ϕ_{BO} = ASYMPTOTIC VALUE OF ϕ_{Bn} AT ZERO ELECTRIC FIELD
ϕ_O = ENERGY LEVEL AT SURFACE
$\Delta\phi$ = IMAGE FORCE BARRIER LOWERING
Δ = POTENTIAL ACROSS INTERFACIAL LAYER
χ = ELECTRON AFFINITY OF SEMICONDUCTOR
V_{bi} = BUILT-IN POTENTIAL
ϵ_s = PERMITTIVITY OF SEMICONDUCTOR
ϵ_i = PERMITTIVITY OF INTERFACIAL LAYER
δ = THICKNESS OF INTERFACIAL LAYER
Q_{SC} = SPACE-CHARGE DENSITY IN SEMICONDUCTOR
Q_{SS} = SURFACE-STATE DENSITY ON SEMICONDUCTOR
Q_M = SURFACE-CHARGE DENSITY ON METAL

Schottky Properties:
Clean and Oxygen Terminated Diamond

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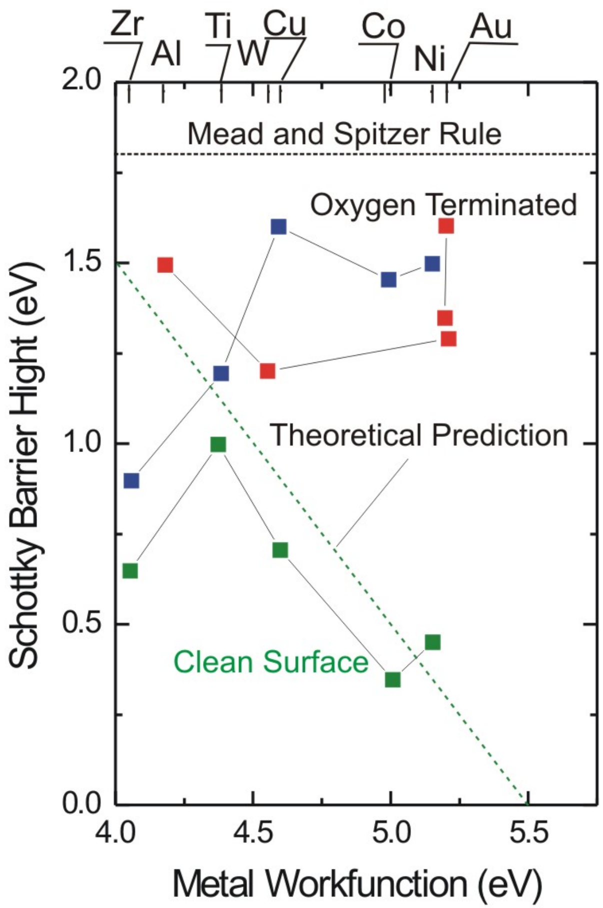

from:
M. Werner, Semicond. Sci. Technol. 18 (2003) S41

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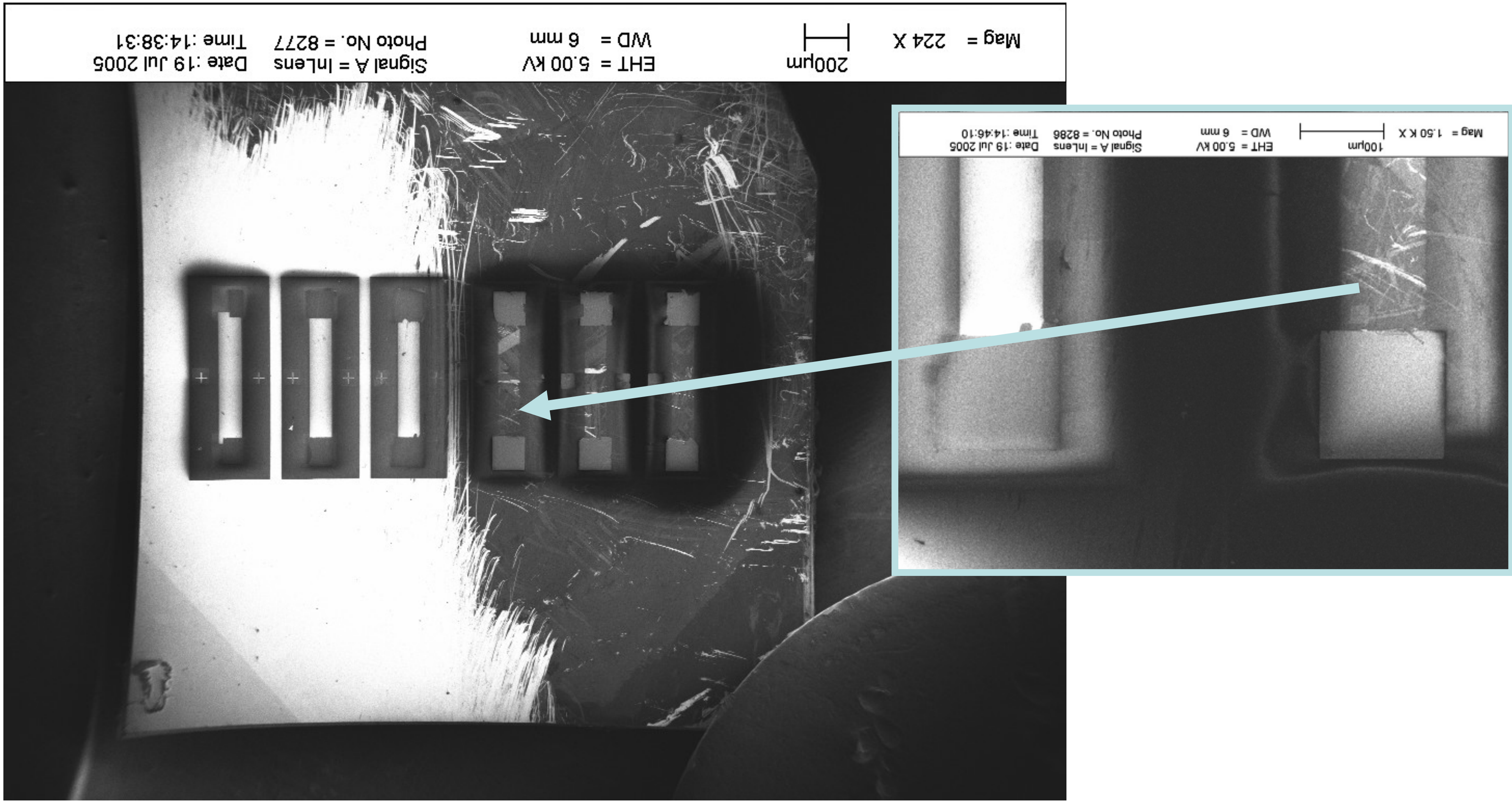
Cleanness: SEM image of Bar-Contact structures



partially wiped
in ethanol

Cleaning by contact mode AFM

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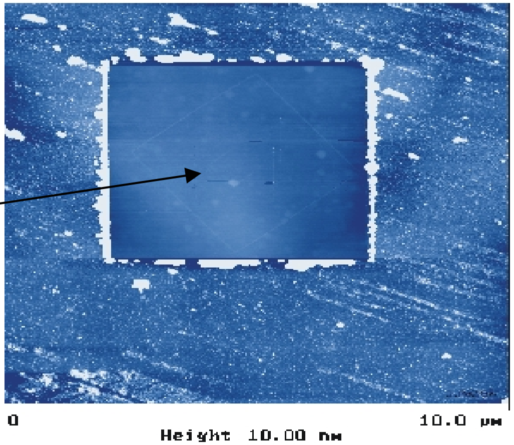
Tapping Mode AFM
Surface Morphology

Contact Mode AFM
Cleanning

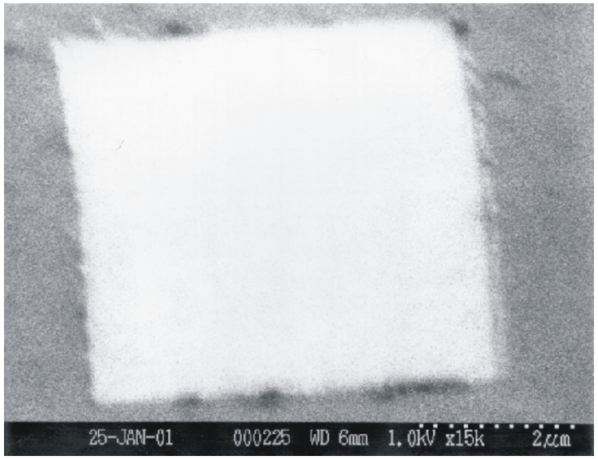
Surface is covered with a thin

(1 -10) nm thick adhesive layer.

AFM Image

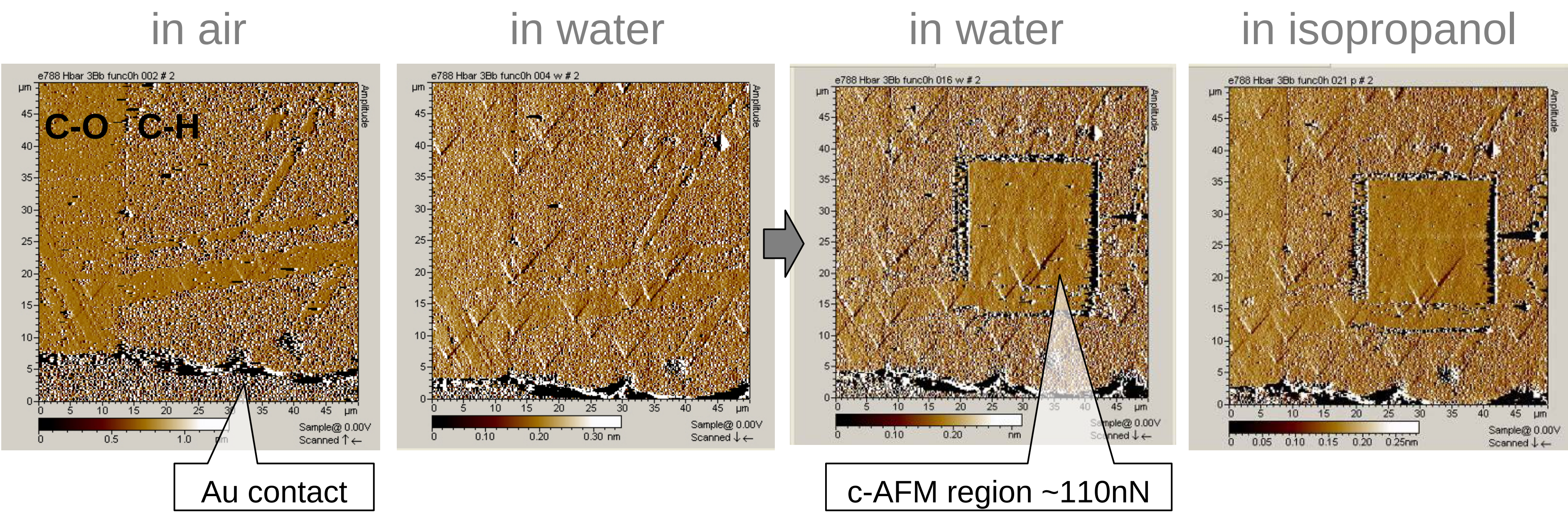


SEM Image



B. Rezek, C.E. Nebel, M. Stutzmann
Diam. and Rel. Mat. 13, 740-745 (2004)

AFM – carbon deposit in air and liquids

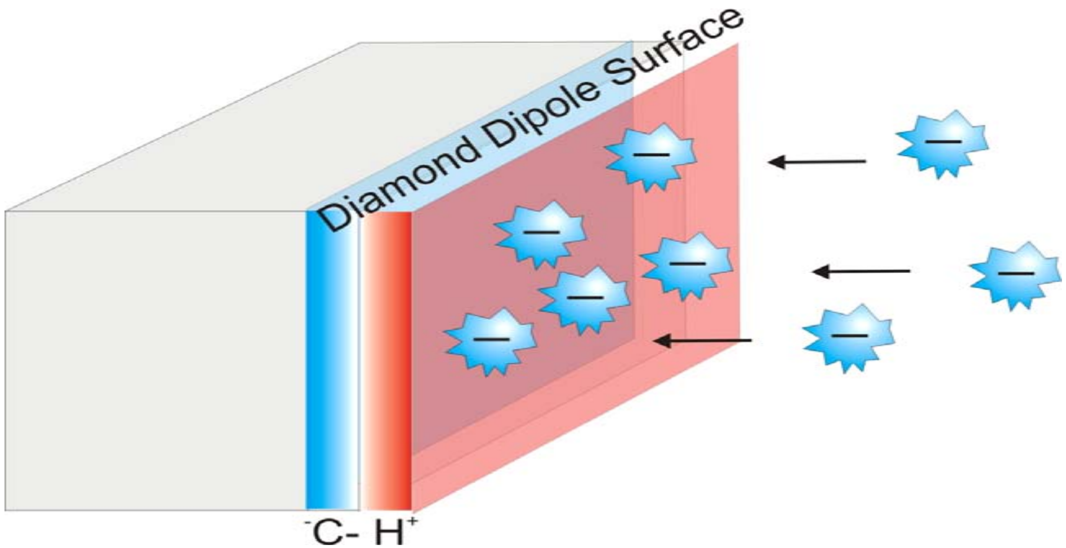


Surface layer is also attached to diamond in:

- Water
- Isopropanol
- not removable by ultrasonic cleaning

Electrostatic Attraction of Ionized Nano-Particles

Accumulation of charged particles
on the surface, in the
water adsorbate?



Due to electrostatic
force,
only small particles
will be attached

•CH Dipole

•CO Dipole

Summary Surface:

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H-terminated Surface

- Technique: H-plasma, H-hot filament
- Unpinned Surface Fermi Level
- Best interface for Schottky Metal Contacts
- In air not stable

Diamond surface oxidation:

- Techniques: wet-chemically (OH), electrochemically (OH), plasma (O)
- Not fully characterized with respect to:
  Degree of termination,
  Surface defect density and distribution

Clean diamond surface

- Realized only in UHV at T > 800 C
- Missing Data about:
  Stability in air,
  Defect density

Roadmap Surface Optimization

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Polishing causes surface damage (not yet characterized!)

Optimization:

1) Polishing
2) Plasma Etching
3) Homo-Epitaxial Overgrowth
4) H-Termination

Bulk Properties

Hole Mobilities

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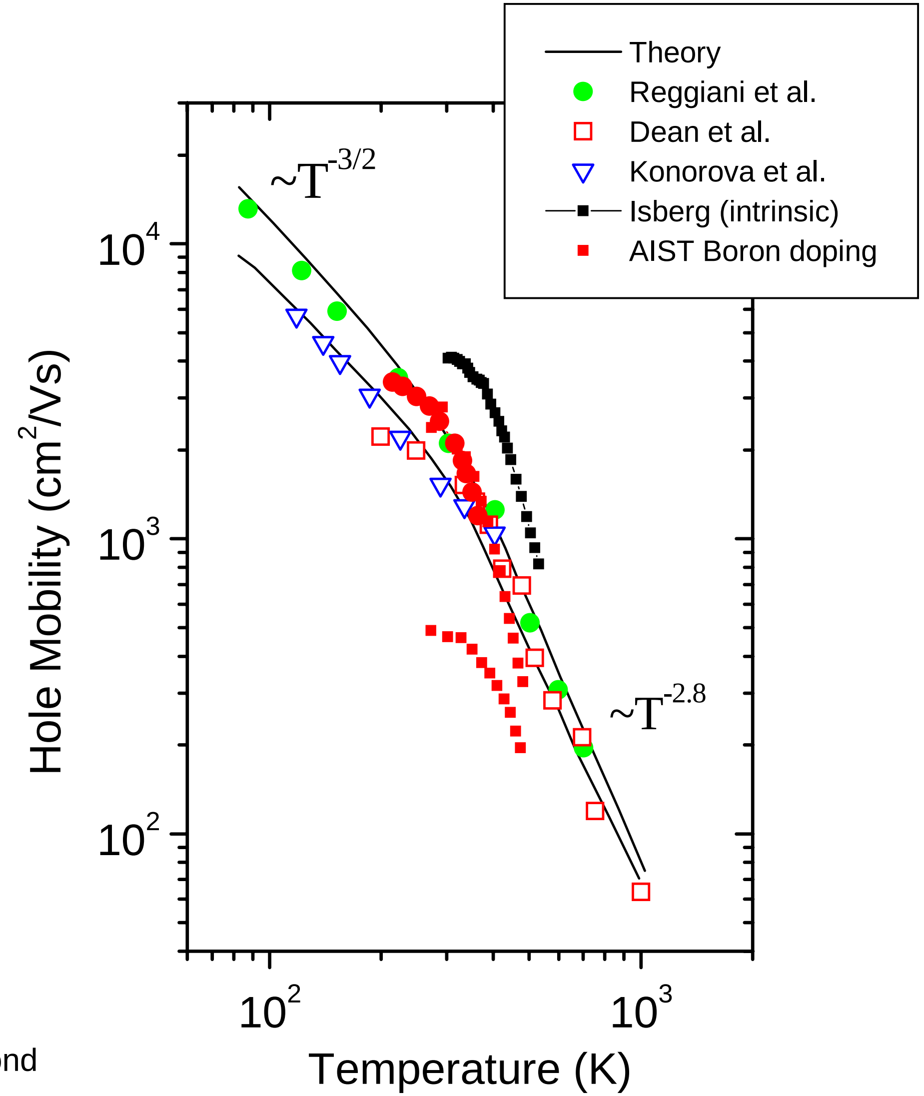
$T^{-3/2}$: acoustic phonon scattering

$T^{-2.8}$: optical phonon scattering



Isberg et al. : time-of-flight on undoped CVD diamond

(Science 297, p. 1670 (2002): **3800 cm²/Vs**)

Reggiani: Time-of-flight on undoped natural diamond

Dean and Konorova: Hall Mobilities

Dr. Okushi et al. AIST: Hall effect on boron doped CVD diamond

Electron Mobilities in natural and P-doped Diamond:

Fraunhofer Institut Angewandte Festkörperphysik

$T^{-3/2}$: acoustic phonon scattering

Isberg et al.,: Time-of-flight in undoped CVD diamond

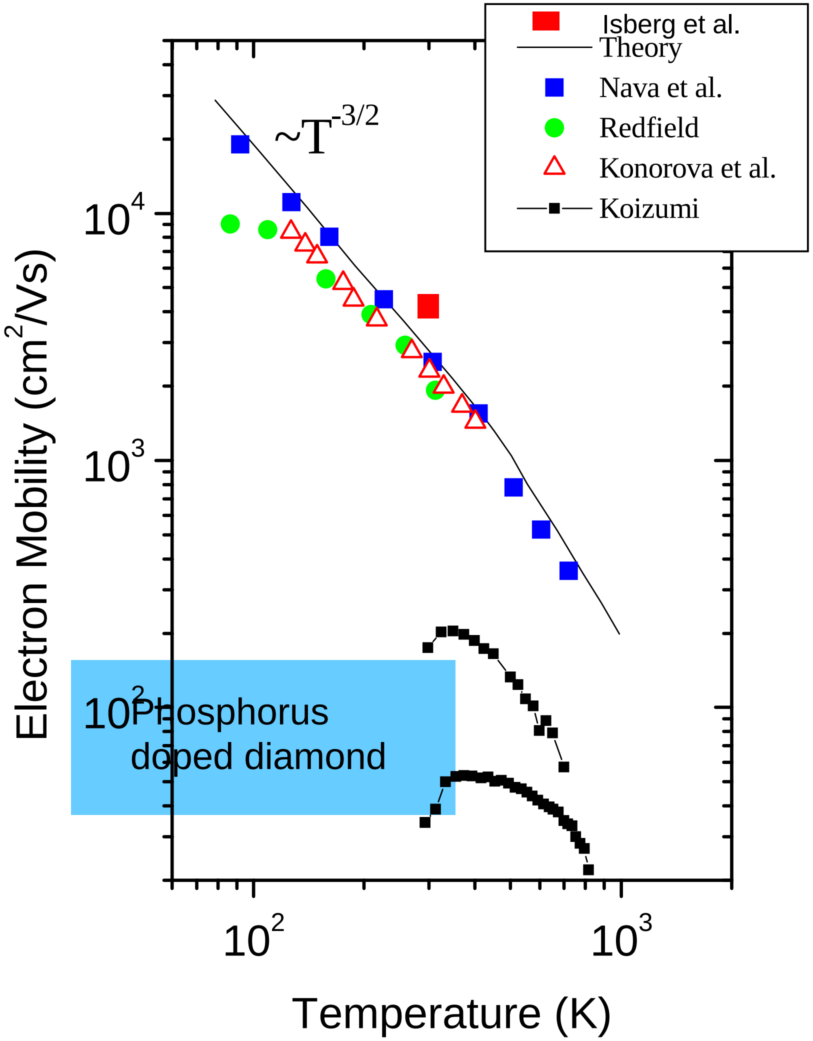
(Science 297, p. 1670 (2002): **4500 cm²/Vs**)

Nava: Time-of-flight on natural undoped diamond

Konorova: Hall effect

Redfield: Hall effect

Koizumi et al.: Hall effect on Phosphorus doped diamond



Defects: H1 Center (g = 2.0028)

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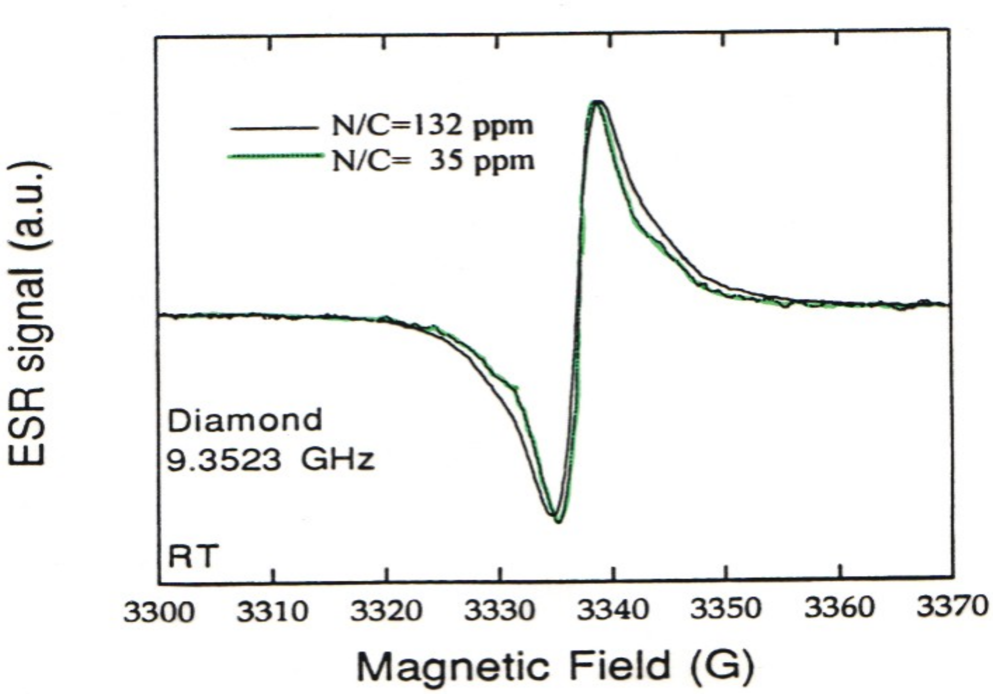
IAF

In homoepitaxially grown single crystalline diamond:

Typical Density: $5x10^{18}$ cm^{-3}

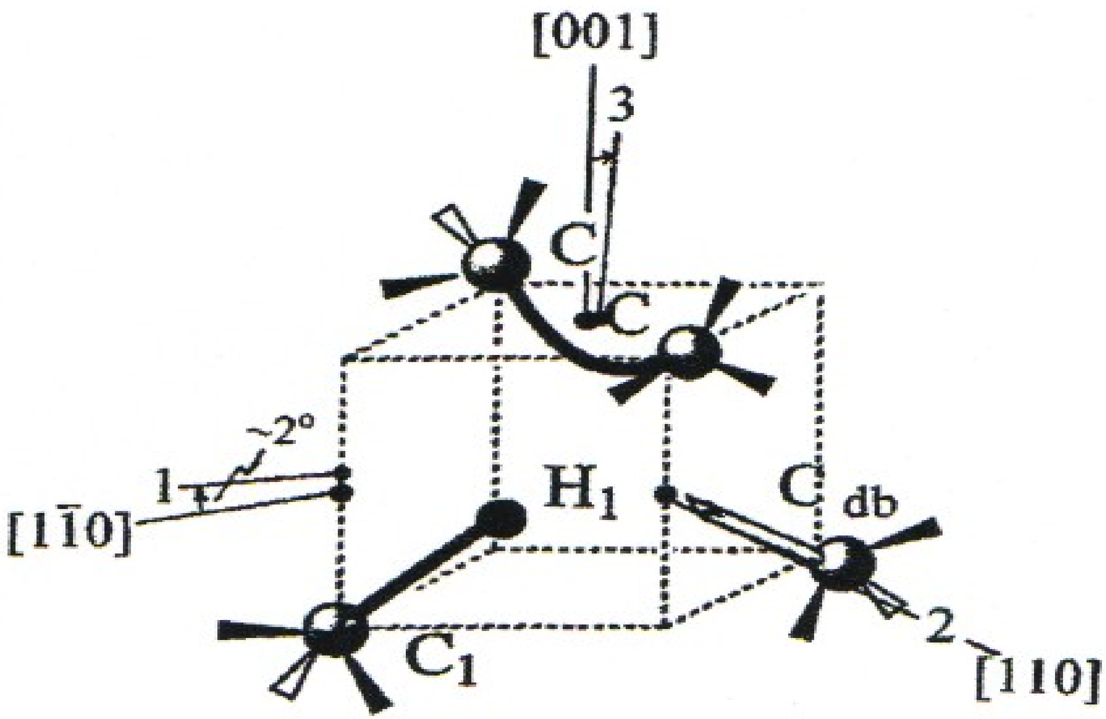


Effect on transport and recombination not clear!

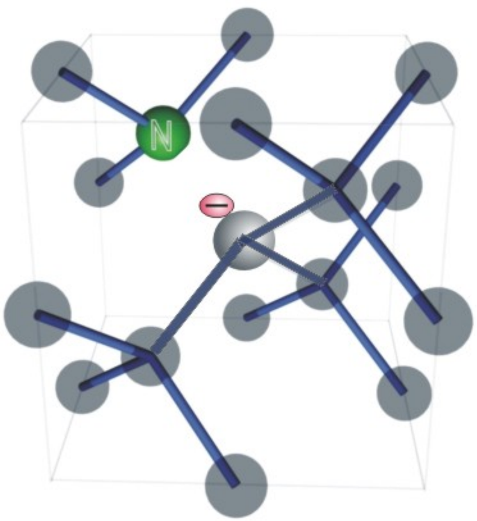
Zhou et al. PRB 54 (1996) p. 7881

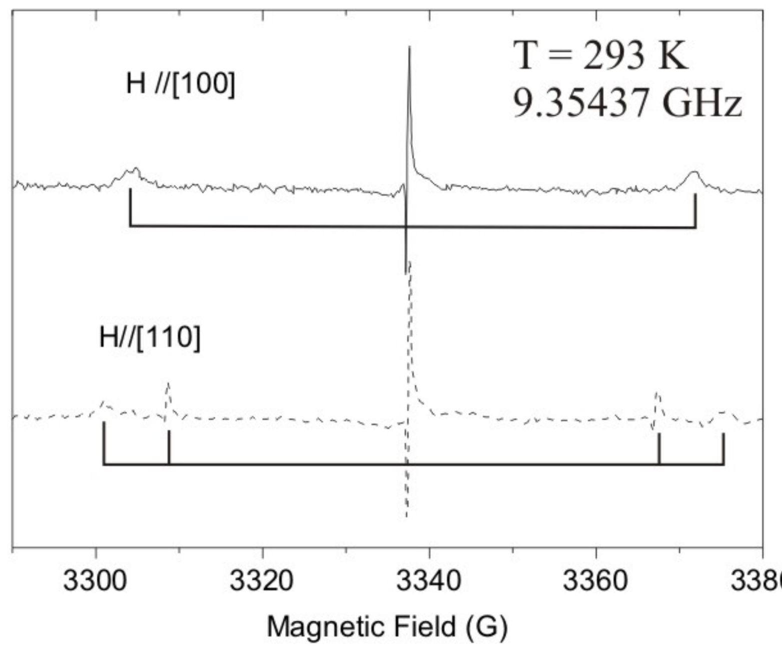
N. Mizuochi et al. DRM .

Defect Model: X. Zhou, G.D. Watkins et al. PRB 54 (1996) p. 7881



Defects: P1 Center (N-Dopant, g = 2.0024)

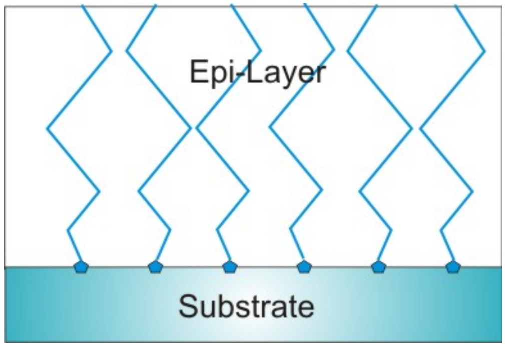




EPR of substitutional nitrogen (g=2.0024).
Satellite positiondepends on magnetic field with respect to (111)-orientation

Dislocations

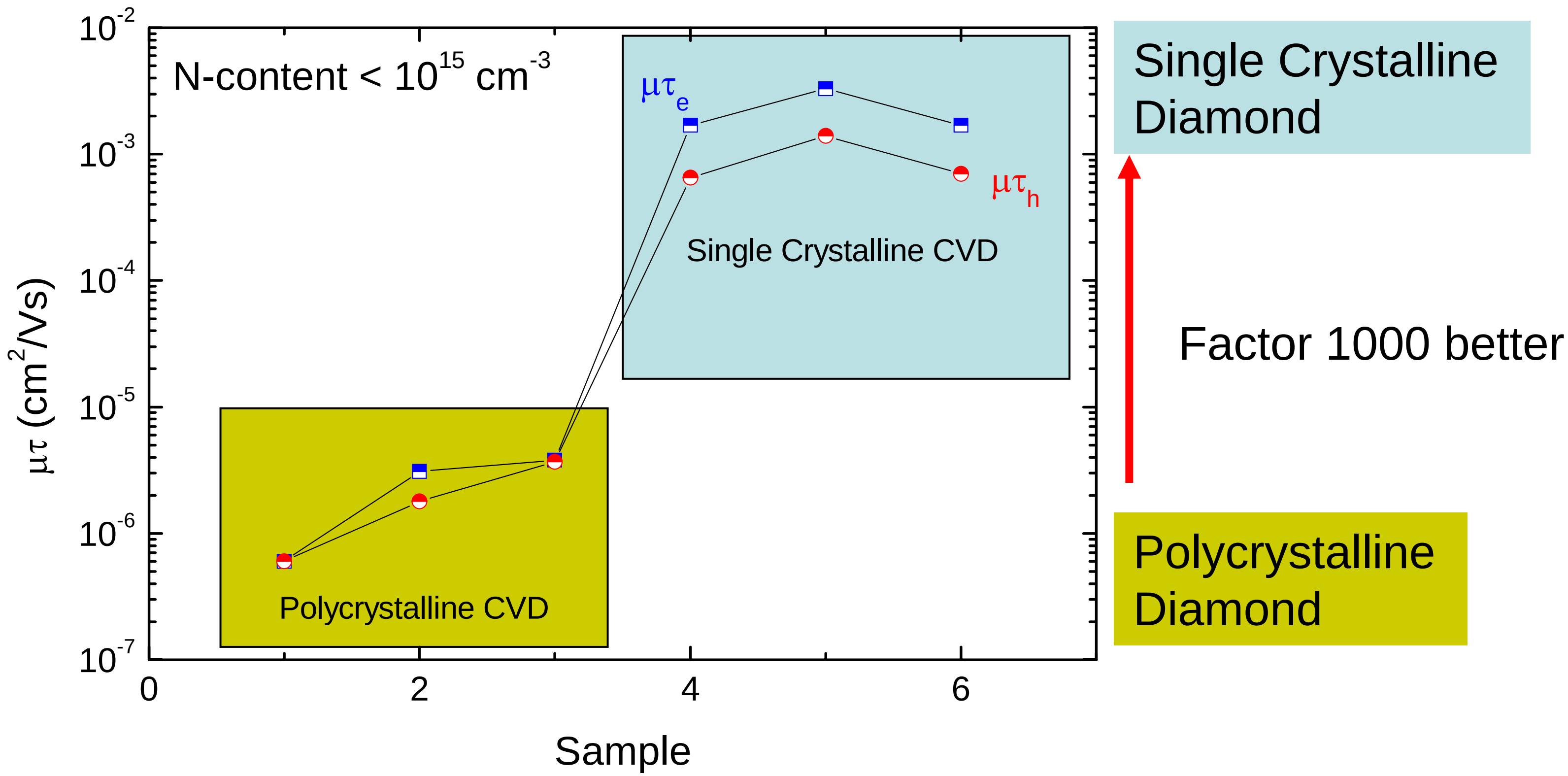
- lattice distortion
- grow from substrate into epi-layer
- killer of high voltage devices



- Minimization:

  soft etching of substrate befor growth , to remove distortions

μτ –Product as Function of Morphology



J. Isberg et al., Diam. Rel. Mat. 13 (2004) 872.

μτ-Product as Function of Nitrogen Content

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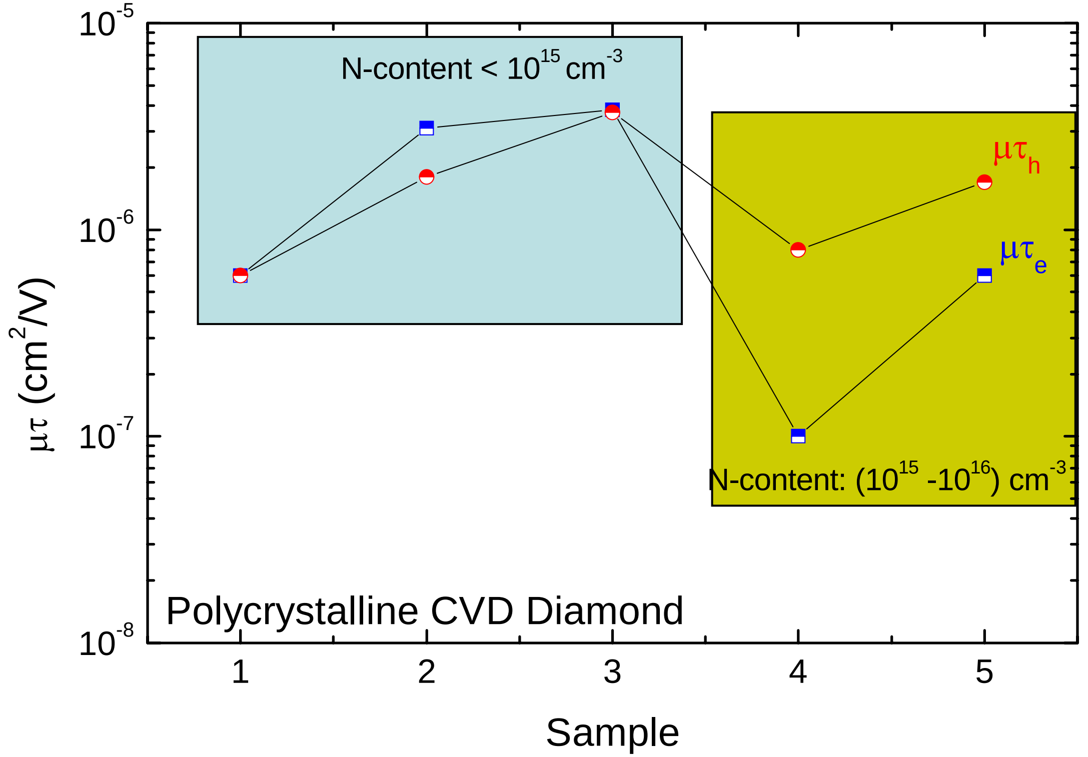
Nitrogen not important



J. Isberg et al., Diam. Rel. Mat. 13 (2004) 872.

Comparision of structural properties:

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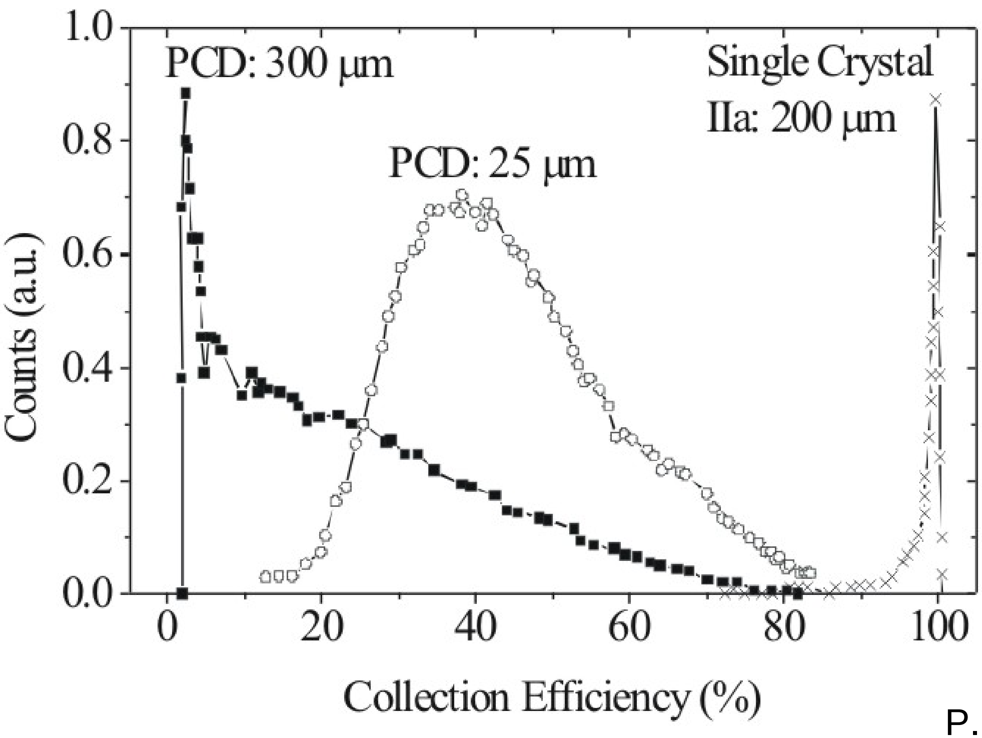
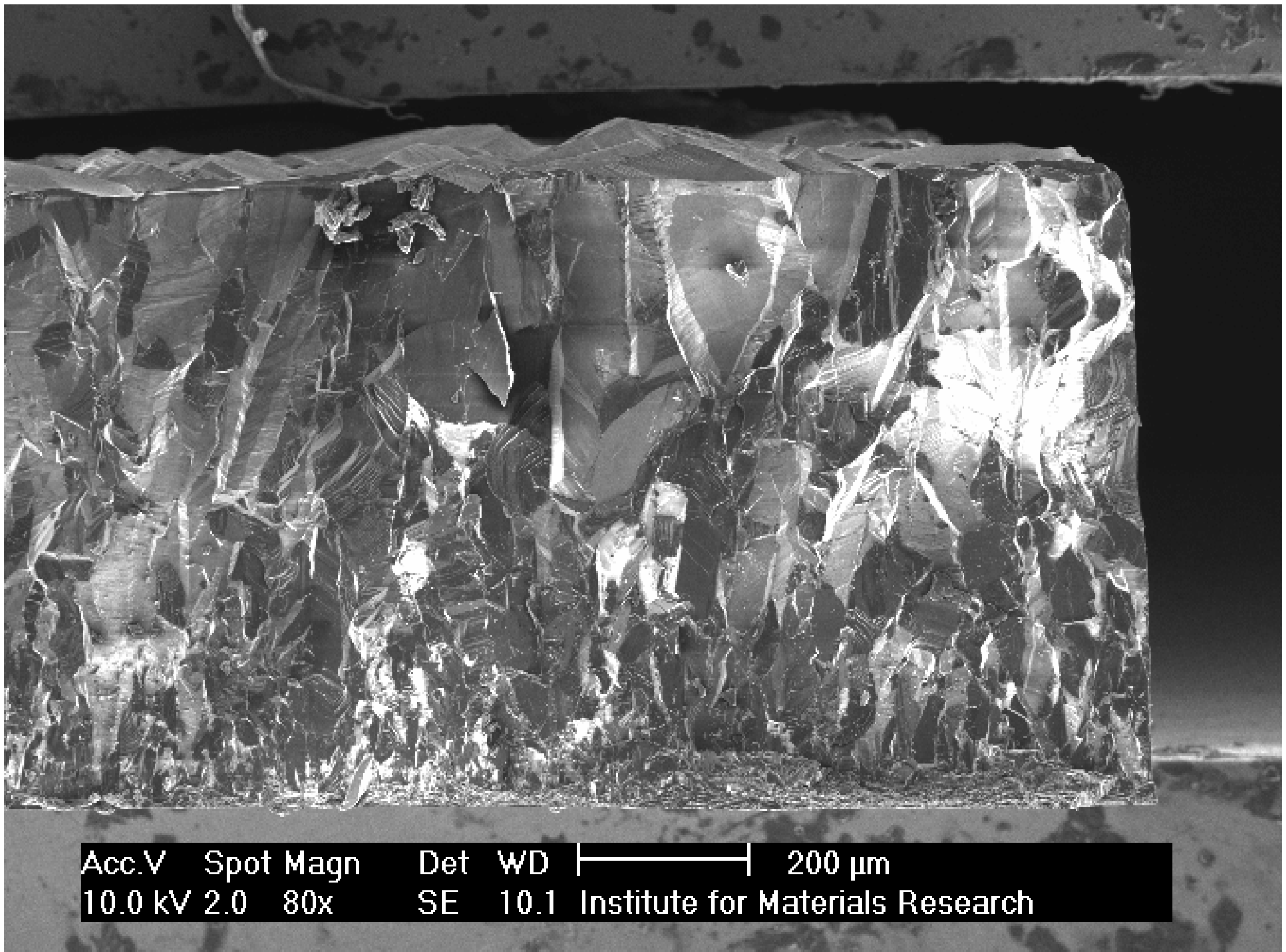


P. Bergonzo et al. 2001

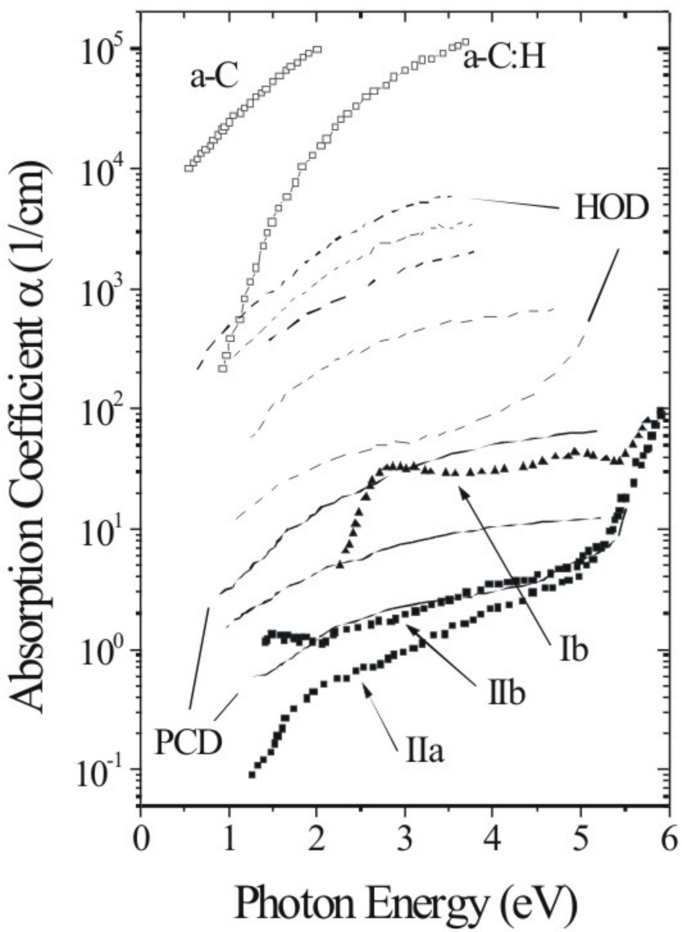
Grain boundary effect: best SCD

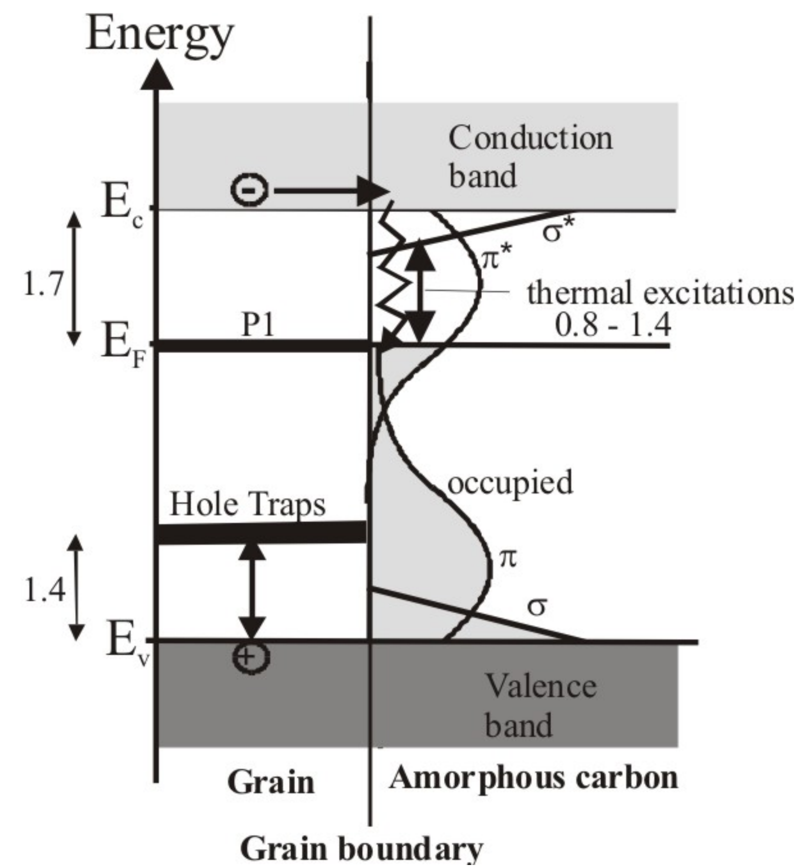
Polycrystalline CVD Diamond



Polycrystalline CVD Diamond

Fraunhofer IAF
Institut Angewandte Festkörperphysik





Deep trapping of carriers (electrons and holes)

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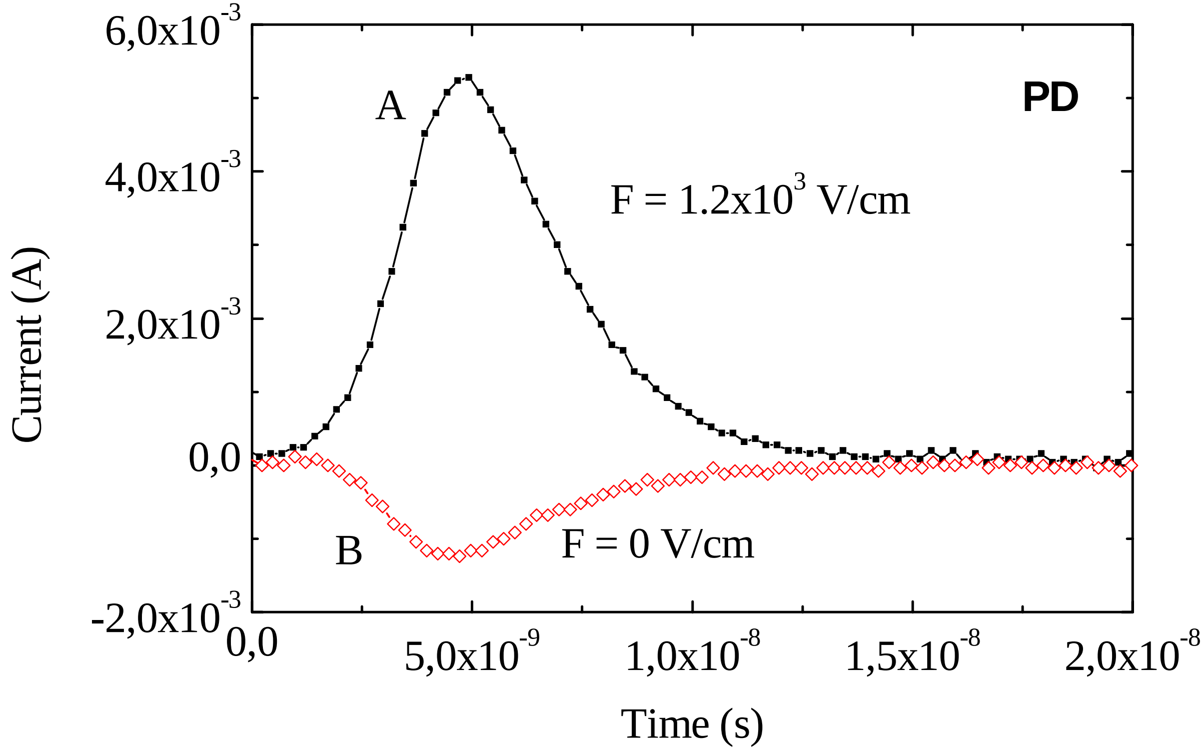
Festkörperphysik

Memory Effect



Model:

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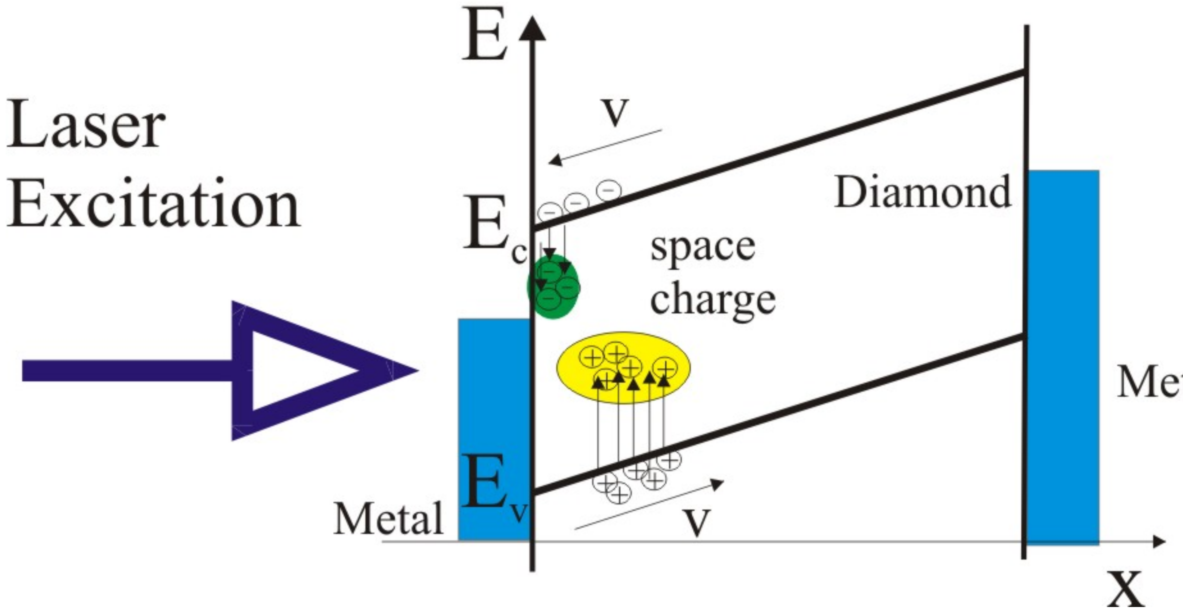
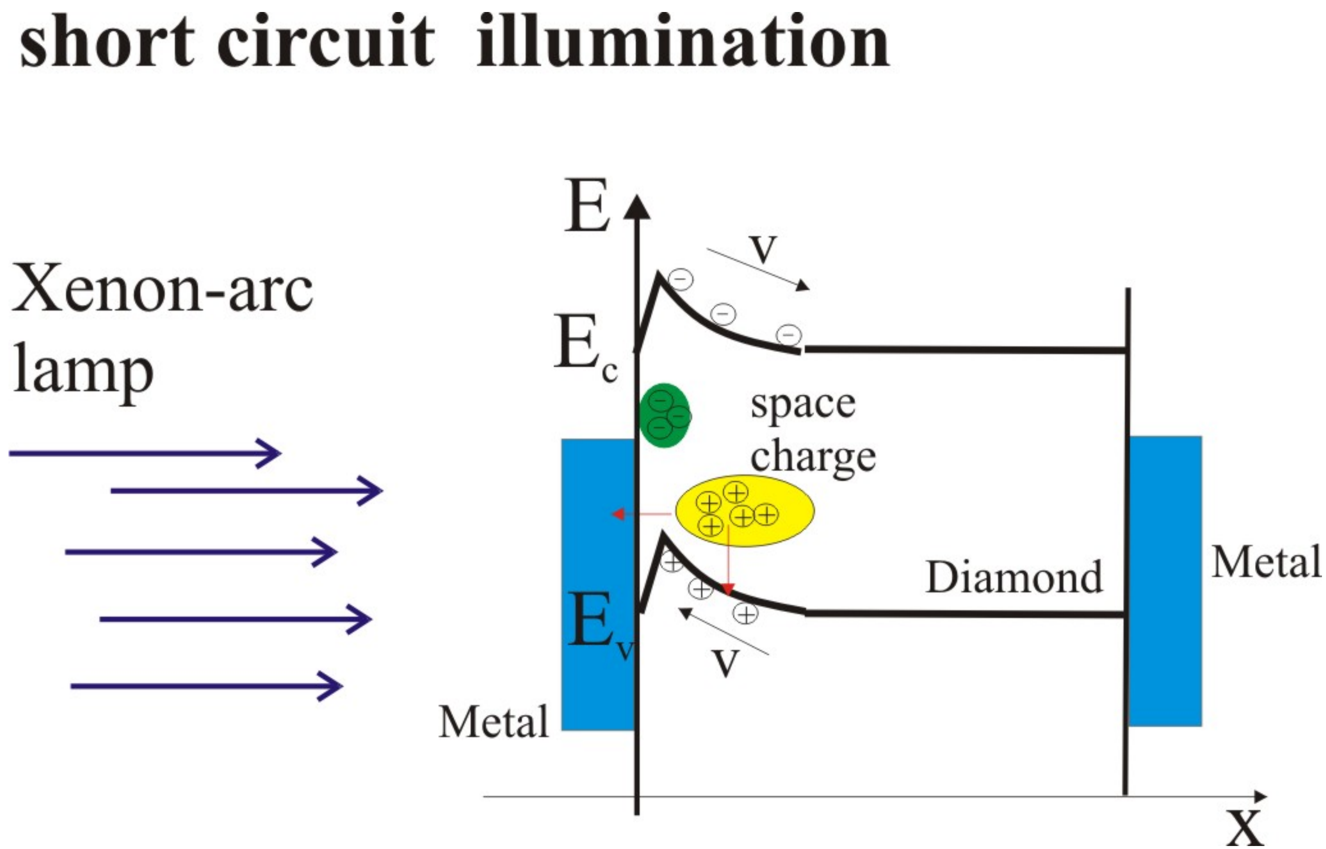
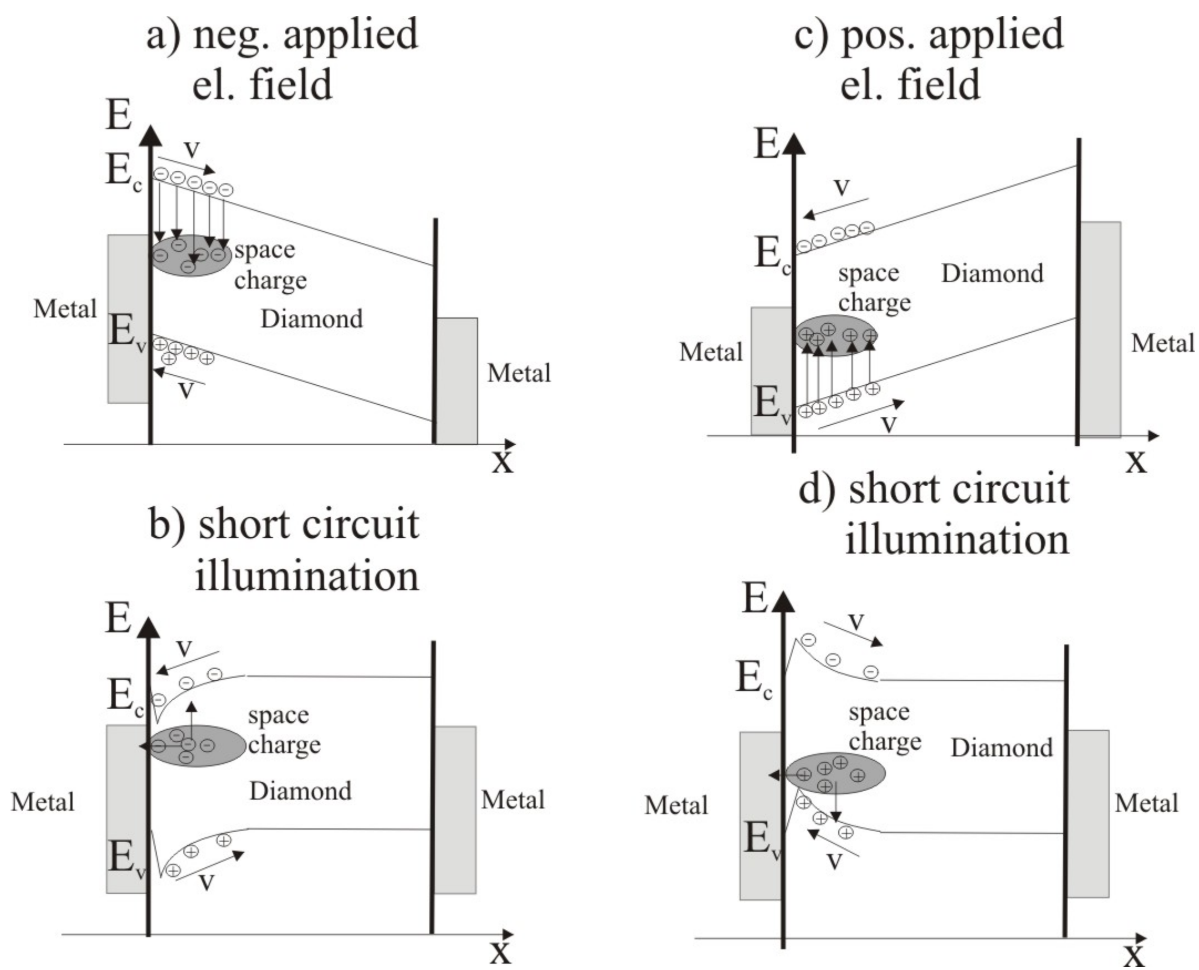
pos. applied el. field



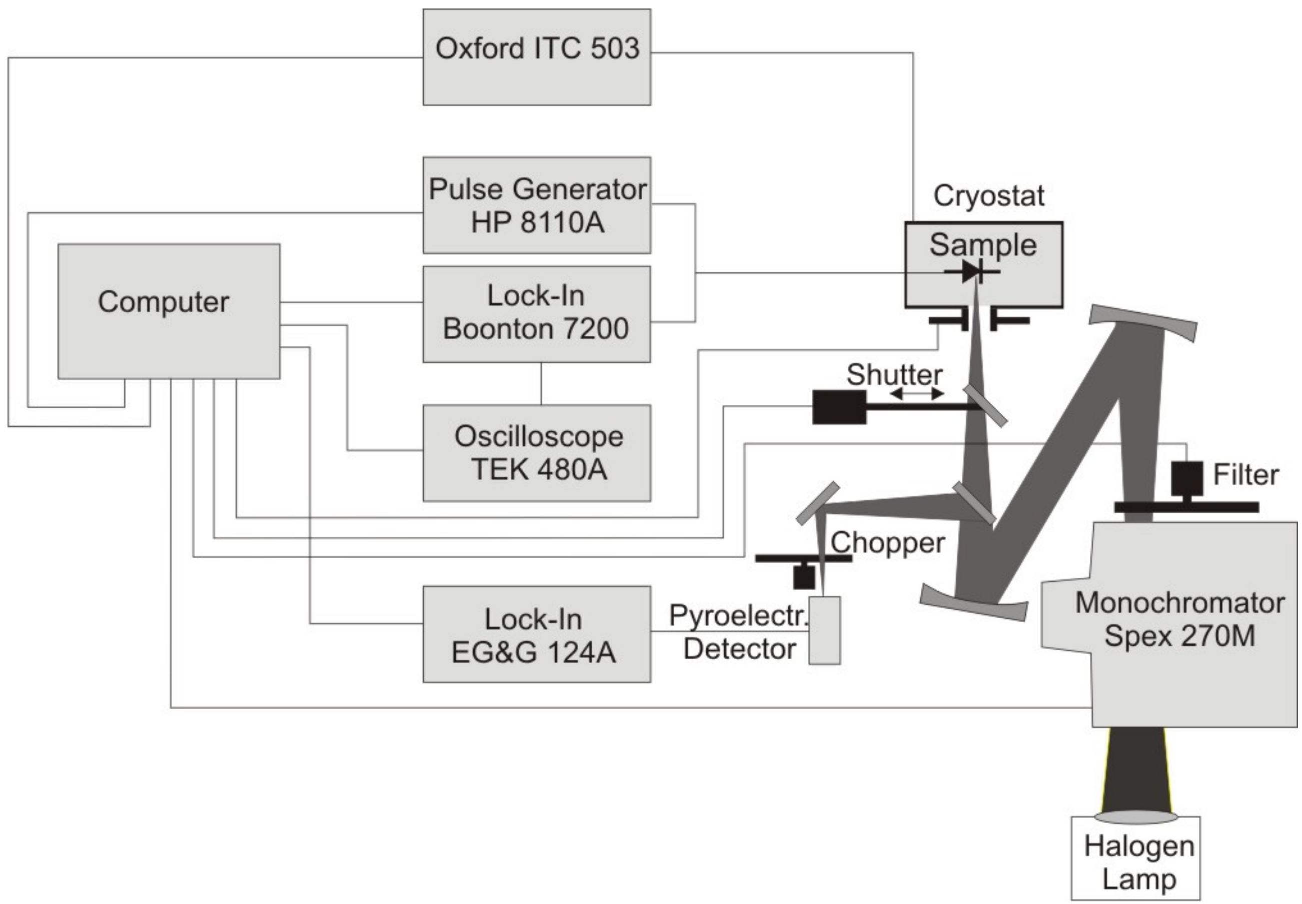
After laser exposure the internal field is reversed:



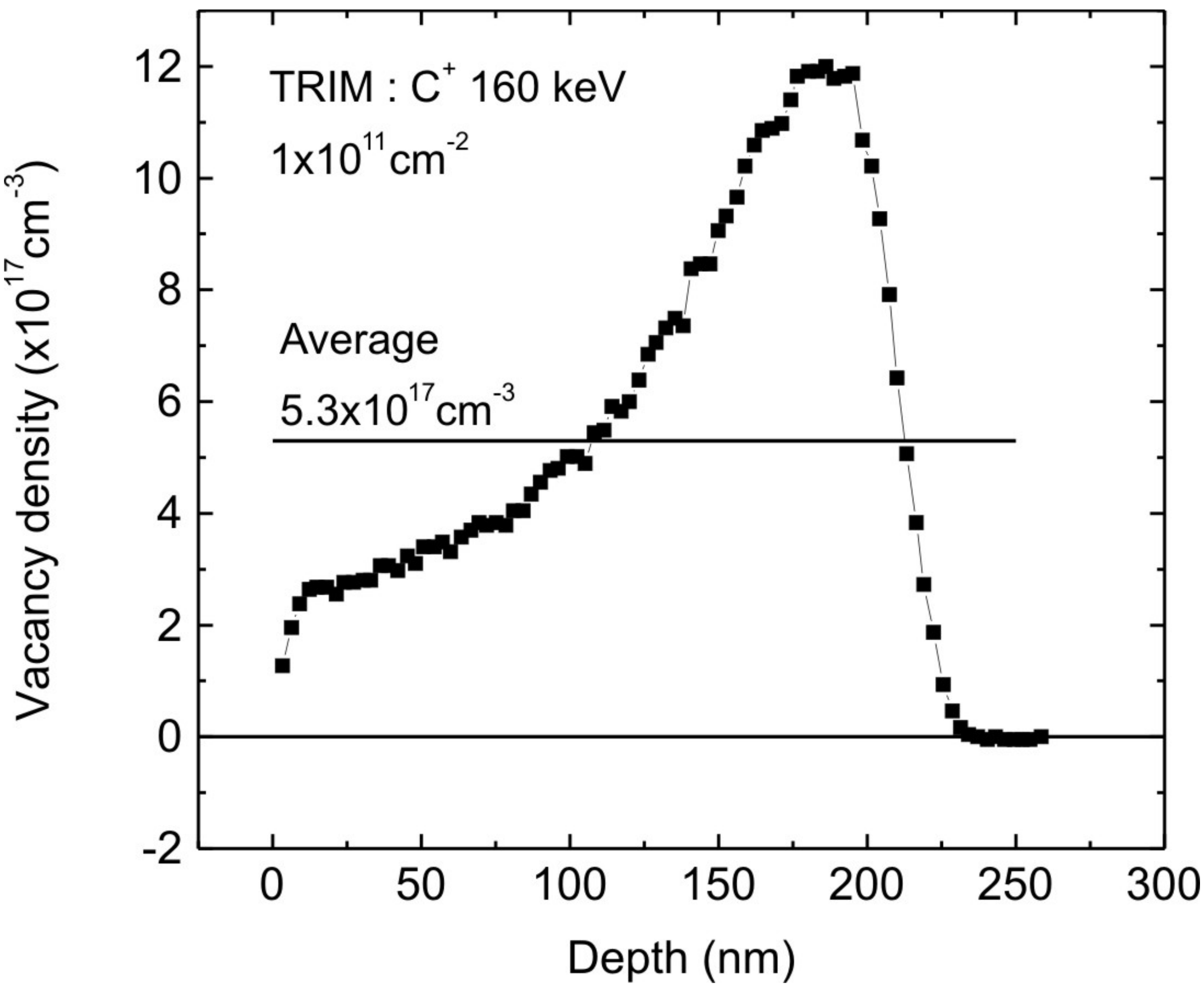
Traps or defect, can be occupied by electrons and holes!



Deep Defect Characterization (ODLTS)



Carbon Implantation



Energy resolved defect variation:

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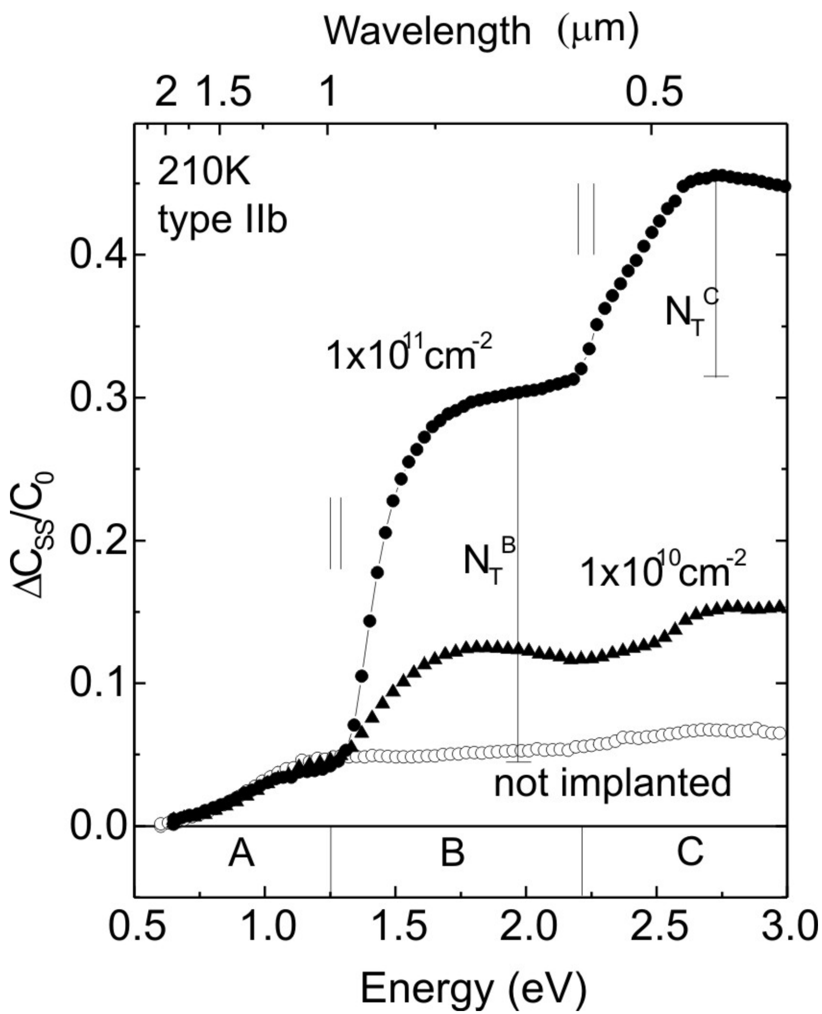
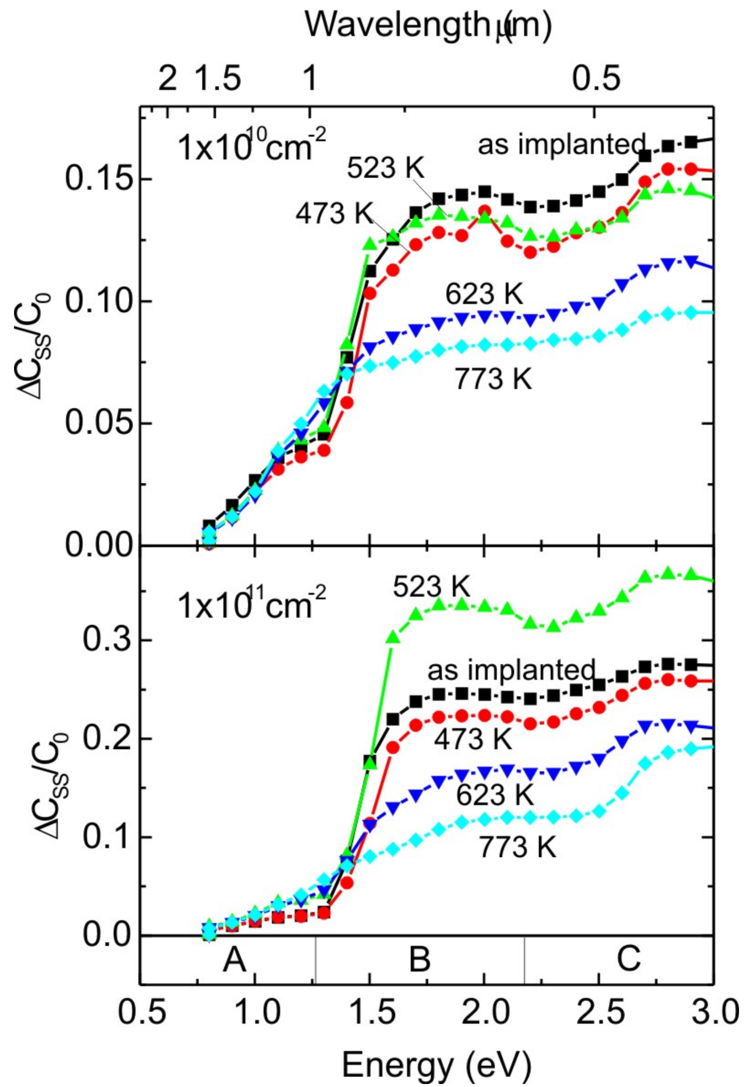
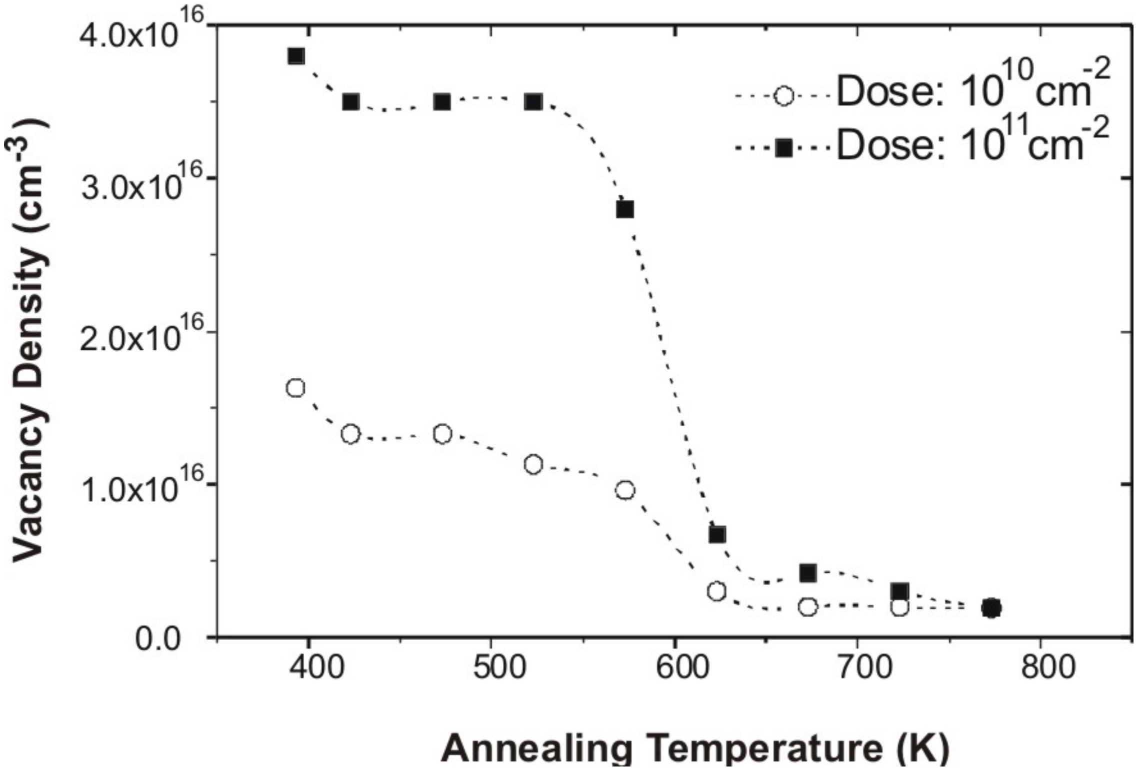


Defect Annealing



Annealing Dynamics: Carbon Vacancy!



T > 600 K

Carbon Implantation induced Defects:

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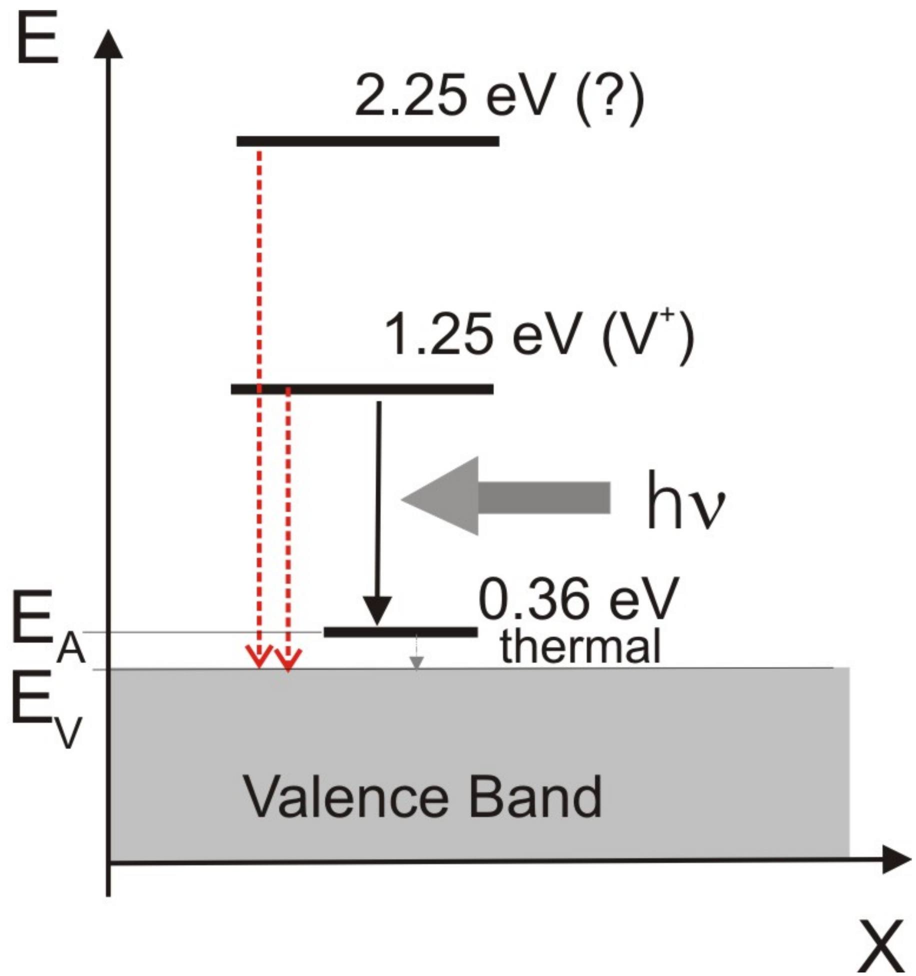

Summay Bulk

- Minor problems from:
  - Defects (H1)
  - Nitrogen (low density)

- Major problems from:
  - Grain boundaries (dislocations?)

Defect characterization not established:

- V
- NV
- NiN
- ....