RAMAN SPECTROSCOPIC INVESTIGATION OF HYDROXYAPATITE

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IMPLANTY 2018
Gdańsk, 28 June 2018

Scope of the presentation

1. Aim of the research

2. Deposition technology

3. Raman spectroscopy

4. Results of investigation

5. Conclusions

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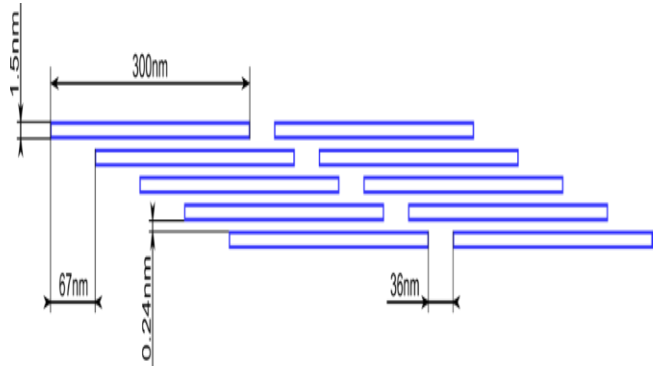
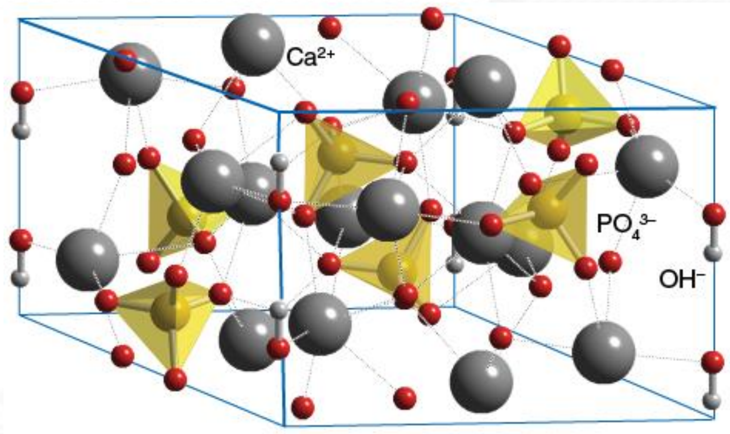
Object

- Titanium alloys (e.g. Ti6Al4V) are widely used as implant materials, however they show only limited corrosion stability and osseointegration in different cases.
- Multilayer protective coating from the internal thin diamond film and a hydroxyapatite (HAp) top coating deposited on the alloy can improve the long-term corrosion behavior as well as the biocompatibility and bioactivity of respective surfaces.
- The internal polycrystalline diamond layer can be deposited e.g. by Plasma Assisted Chemical Vapor Deposition (PACVD),
- HAp coatings were formed in aqueous solutions by electrochemically assisted deposition (ECAD) at varying polarization parameters.
- Artificial HAp coatings should have similair molecular composition to natural bones.

Bone

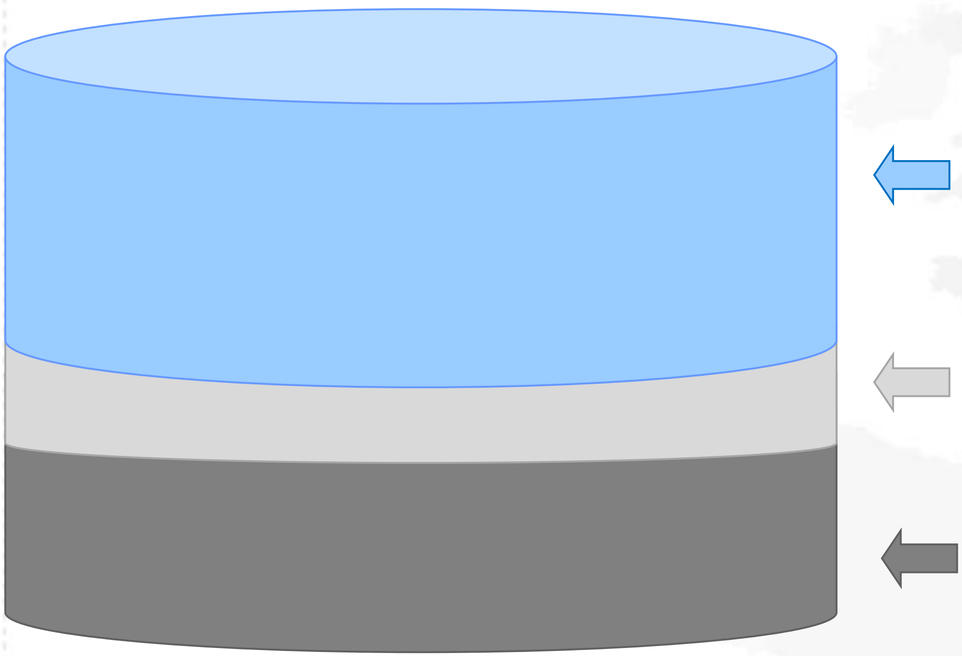




Collagen arranged in the microfibril. The diameters of the proteins and the 0.24 nm spaces between the molecules are disproportionately large for the purpose of the illustration.

Bone implant model

Investigation of diamond and boron doped diamond (BDD) films deposited on titanium-aluminium alloys

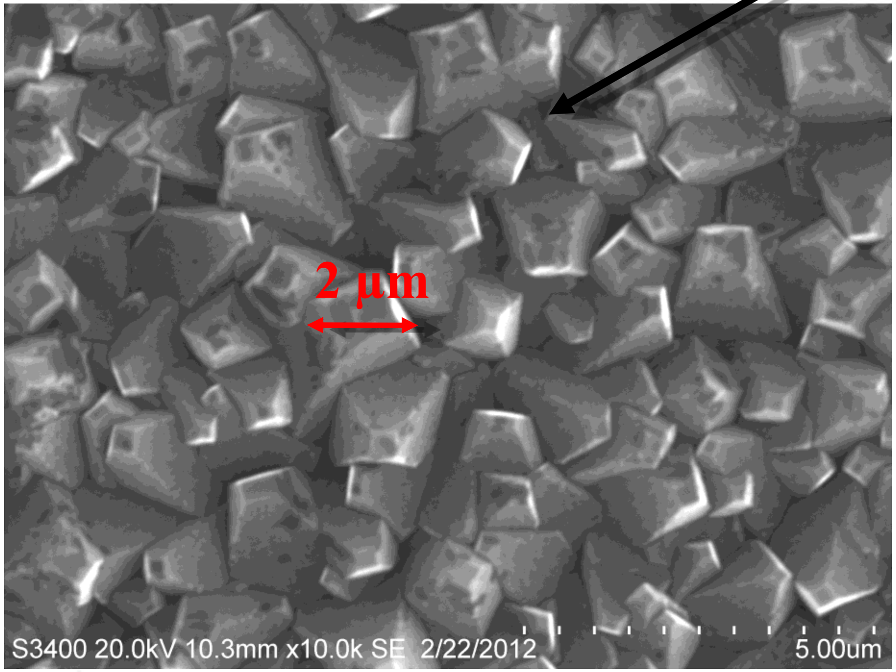


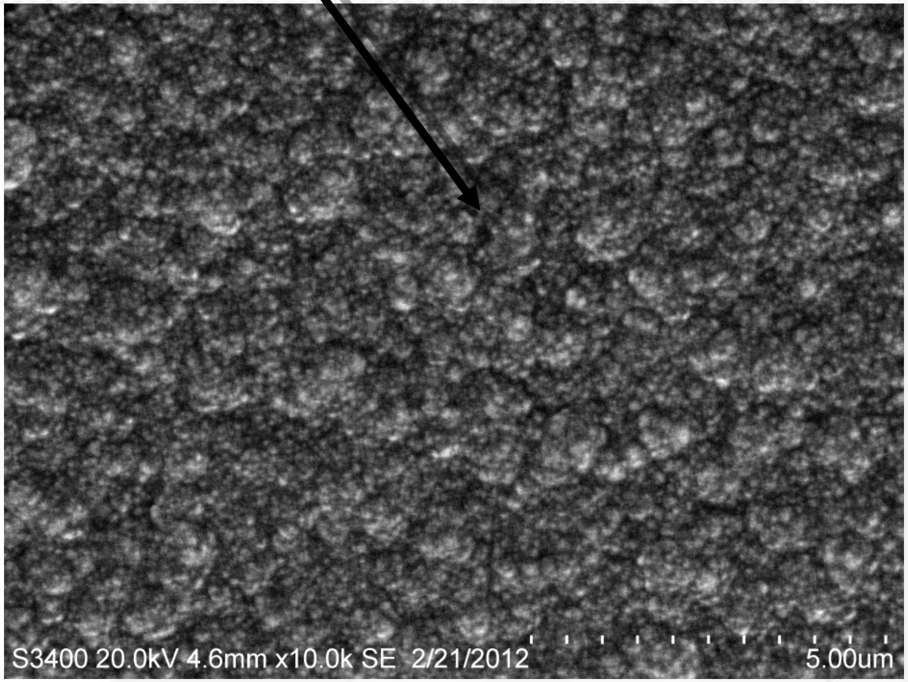
- Microcrystalline Diamond Coating **(MDC)**
- Boron-doped nanocrystalline Diamond Coating **(B-NCD)**
- Nanocrystalline Diamond Coating **(NCD)**

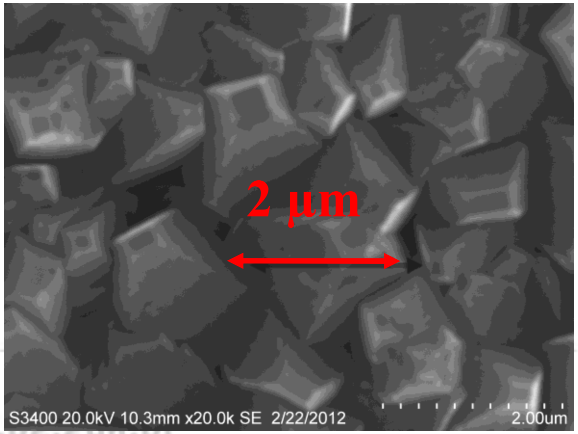
Intermediate structures (amorphous carbon,TiC)

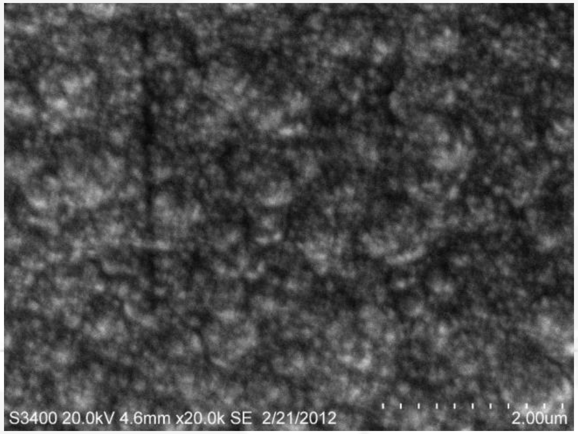
Substrate (Ti6Al4V)

SEM - MCD vs NCD

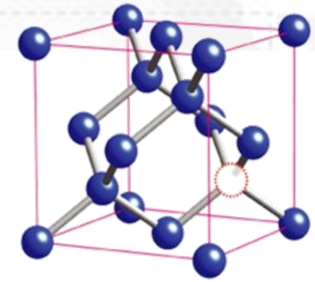








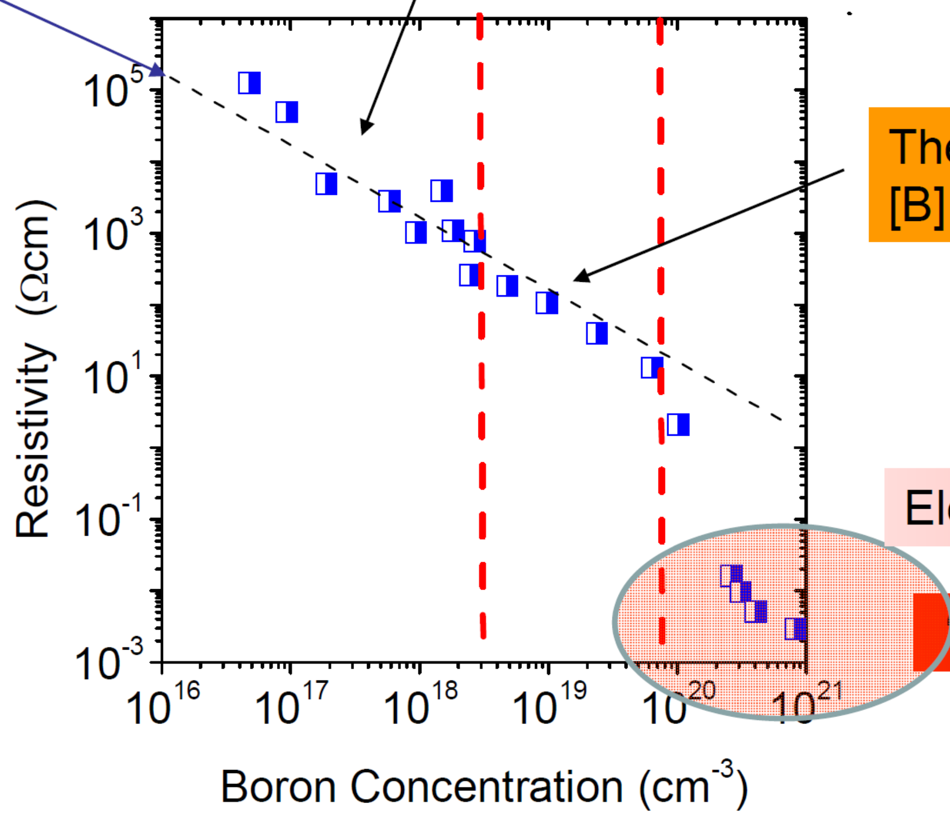
Diamond doping



$\rho \approx (e\mu B)^{-1}$

Extended State Transport up to: $3x10^{18}$ cm^{-3}

Thermal Activated Hopping:
[B] $>3x10^{18} cm^{-3}$



Electrochemical Grade Diamond

"Metallic Doping" $(2\text{-}5)x10^{20}$ cm^{-3}

A. J. Neves, Maria Helena Nazaré, Properties, growth and applications of diamond , INSPEC. EMIS Group - 2001

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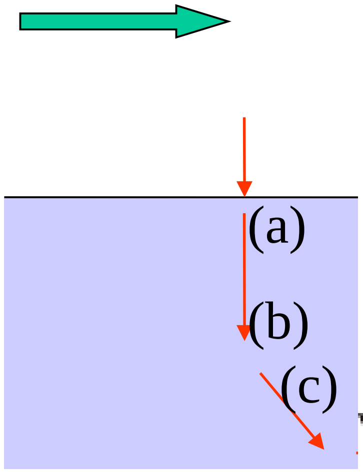
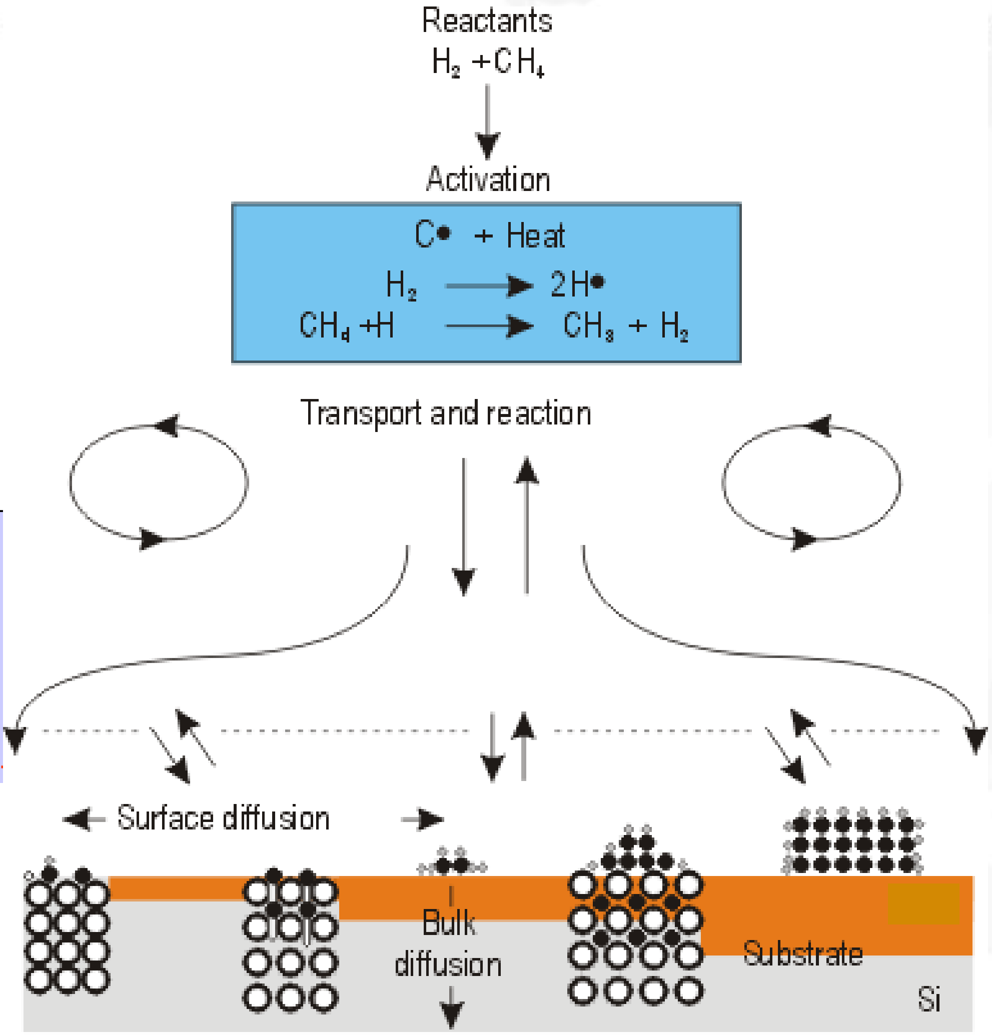
CVD

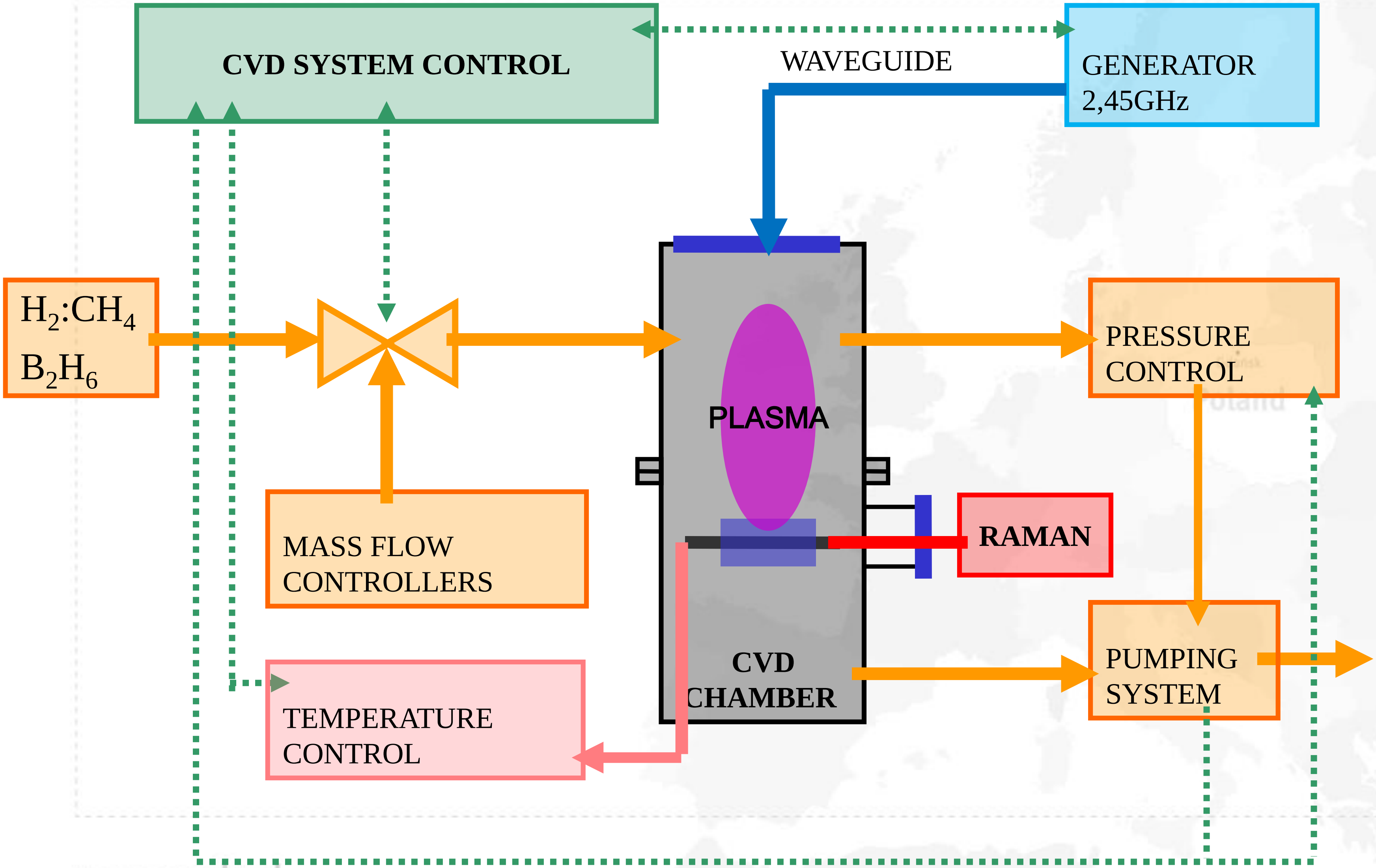
Gazy reaktywne





http://www.postech.ac.kr/mse/tfxs/lecture_2000_1/chapter4.ppt

CVD

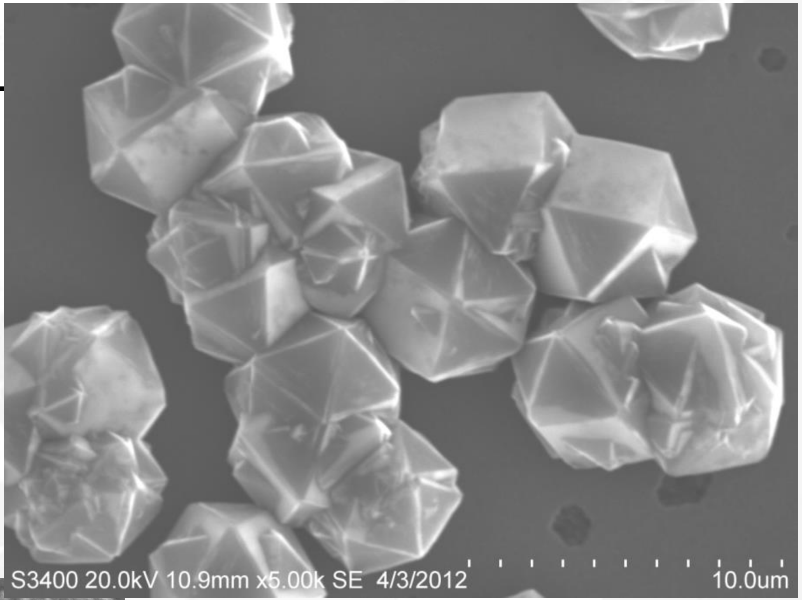

CVD SYSTEM CONTROL
WAVEGUIDE
GENERATOR 2,45GHz
H_2:CH_4
B_2H_6
PLASMA
PRESSURE CONTROL
RAMAN
MASS FLOW CONTROLLERS
CVD CHAMBER
PUMPING SYSTEM
TEMPERATURE CONTROL

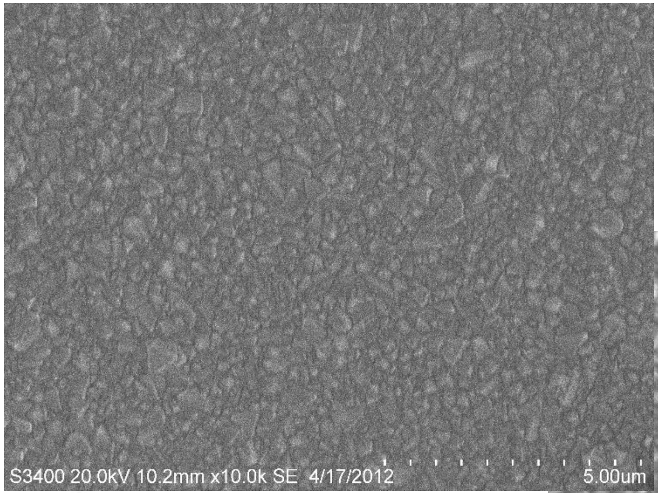
Process

Temperature of substrate	Microwave power	Total pressure	$CH_4:H_2$	Boron doping
500ºC	1300 W	50 Torr	1%	0
or			or	or
700ºC			4 %	5000 ppm

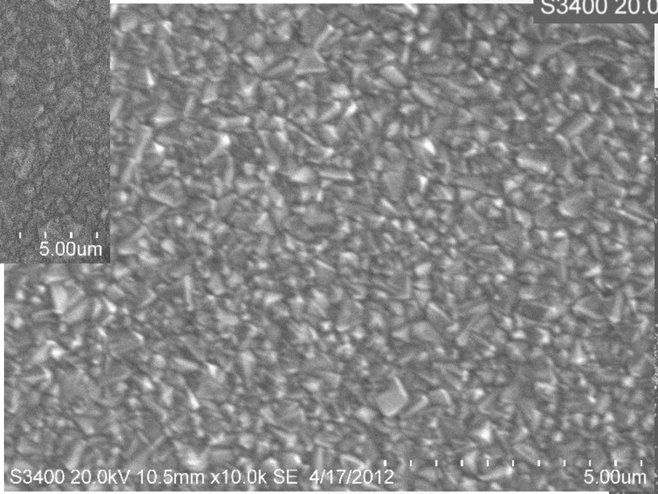
Seeding

- Nanodiamond powder ~(2 nm-150 nm) –
  - Nanodiamonds in water
  - Nanodiamonds in DMSO
  - Mechanical treatment

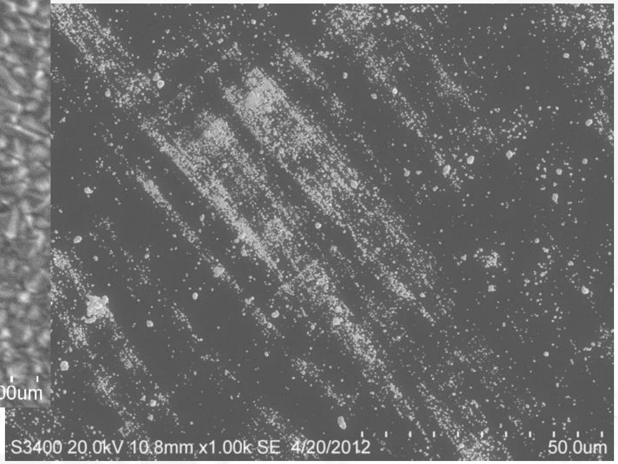




In water

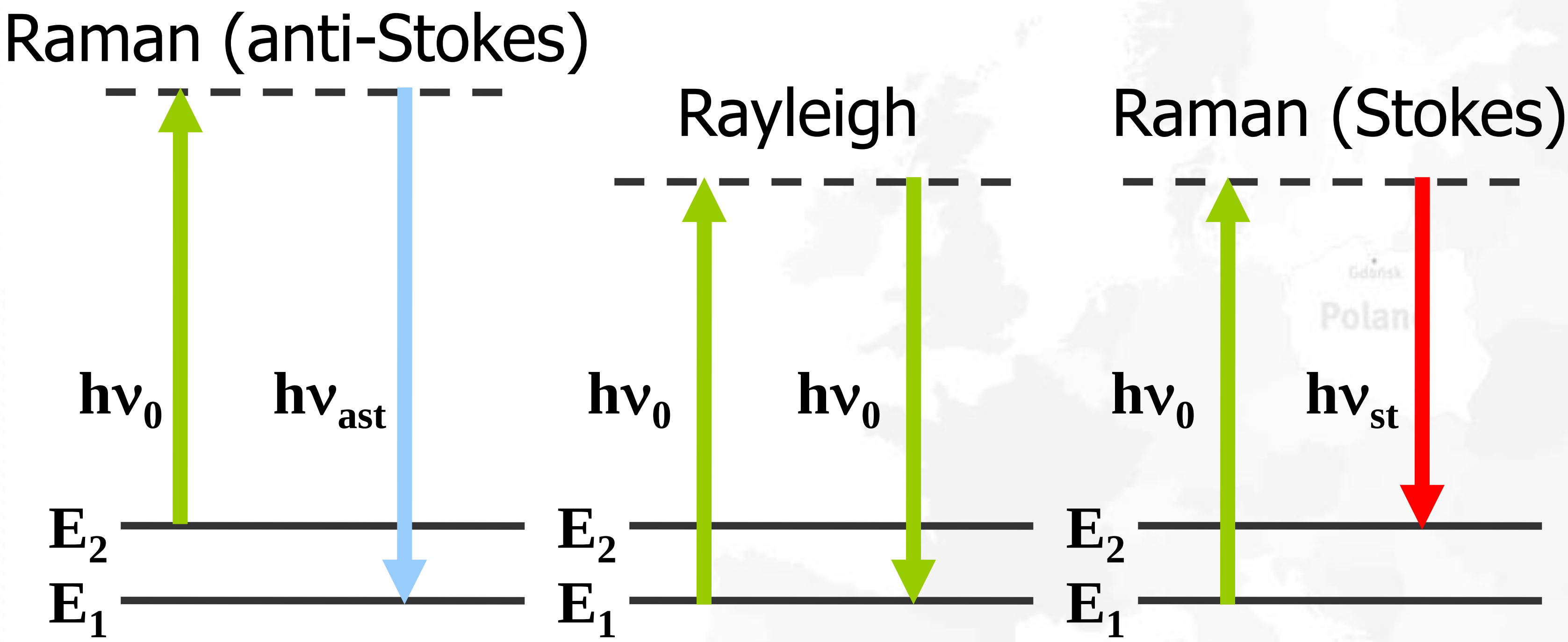


In DMSO



Mechanical

Raman scattering



Raman signal intensity

Dependence between measured Raman intensity I_R [photons per second] and excitation wavelength λ_0:

$$\mathbf{I_R \sim (1/\lambda_0)^4}$$

For a given λ_0, I_R be expressed as

$$\mathbf{I_R = I_L \cdot \sigma \cdot K \cdot P \cdot C}$$

I_L – laser excitation intensity [photons per second]

σ - absolute Raman cross-section [cm^2 per molecule]

K - a constant accounting for measurement parameters

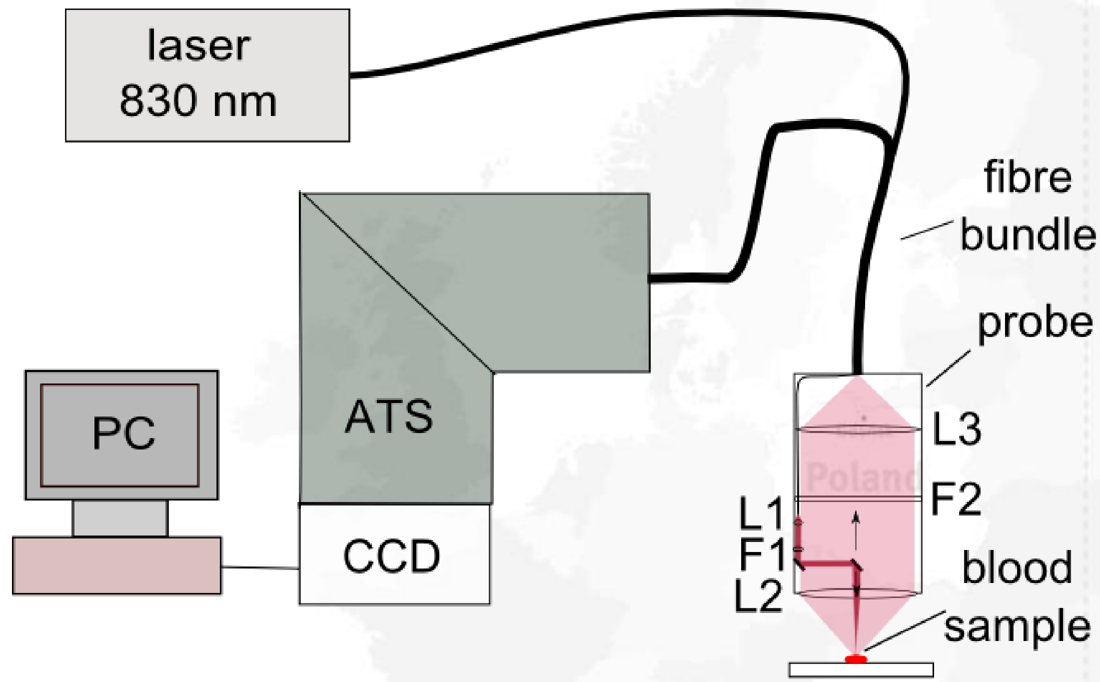
P - sample path length [cm]

C - concentration [molecules per cm^3]

Fiber – optic setup

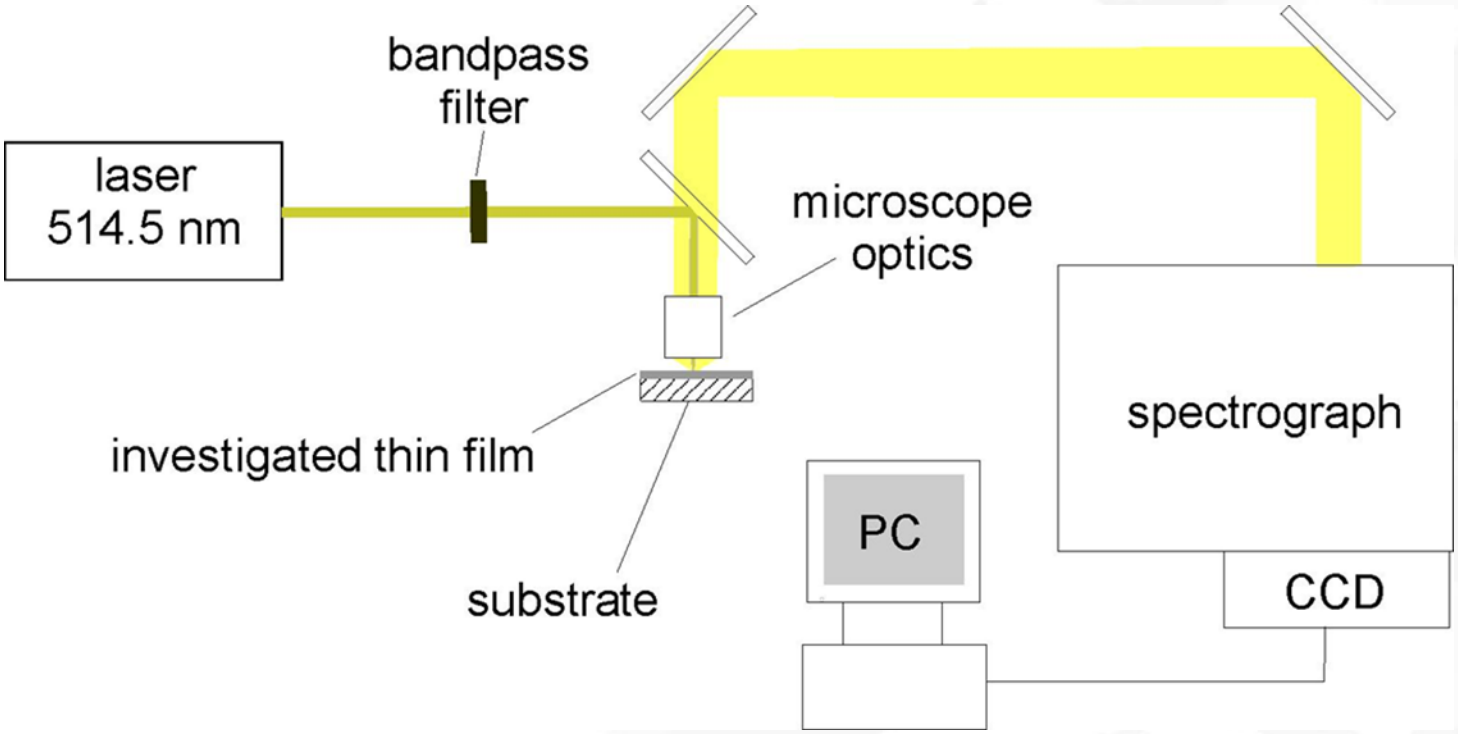
Spectrometer made by VTT Finland Ramstas :

- CW diode laser 830 nm/100 mW on the sample,
- Fibre optic probe, WD = 2.5 cm,
- Dedicated metal sample holders and probe positioning setup



L1,L2, L3 - lenses;
F1- laser line filter
F2- longpass filter;
ATS- axial transmissive spectrograph

Raman microscope



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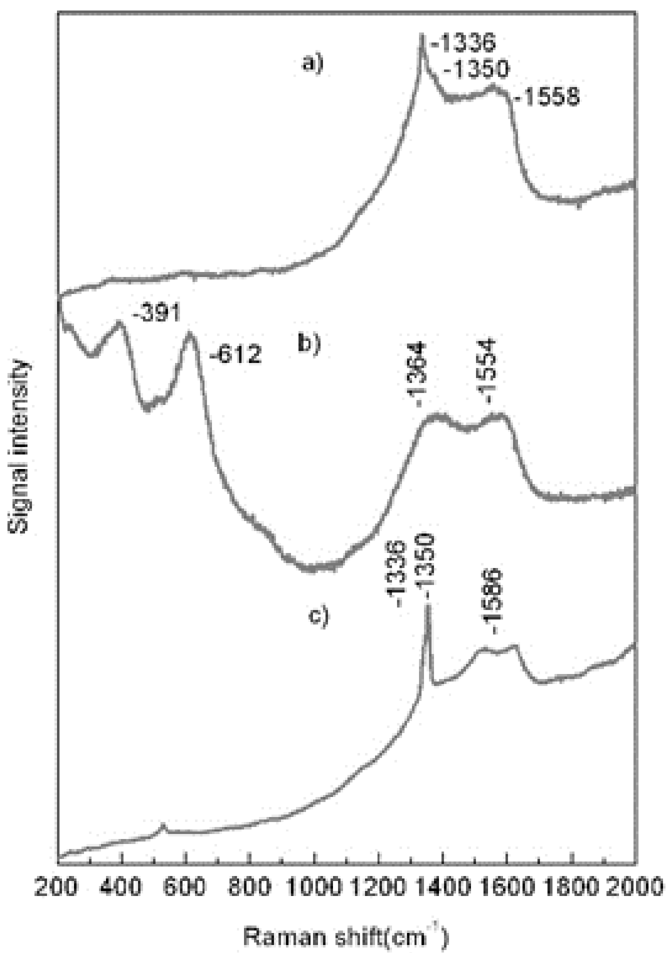
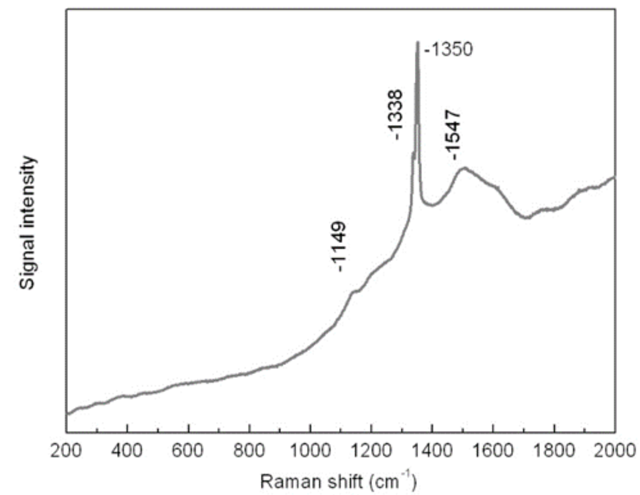
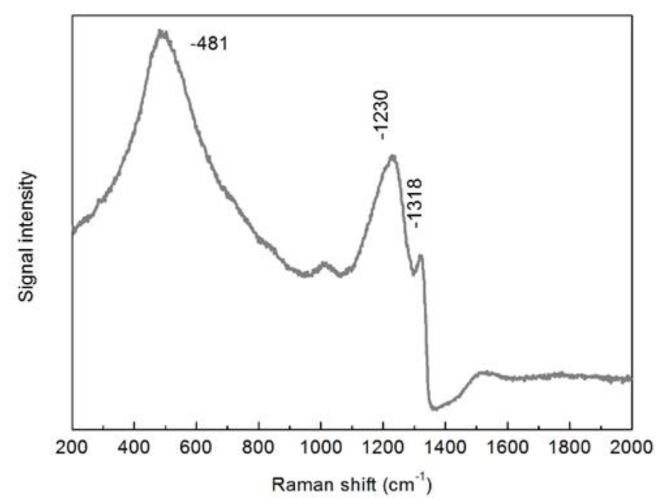
Diamond interlayer







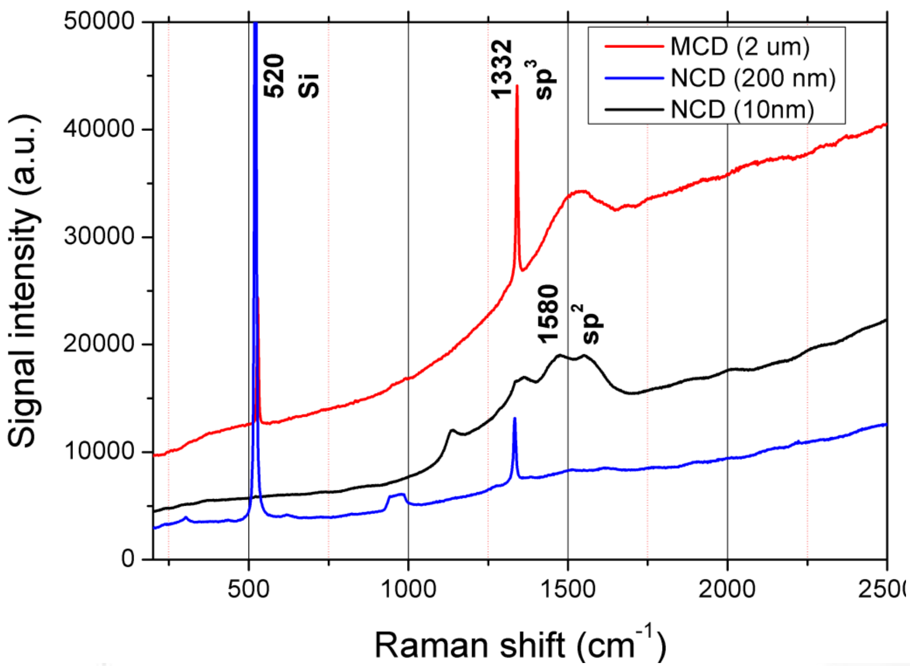
(left)
MCD coatings
(a) prepared after is seeding,
(b) with defect, prepared after is seeding,
(c) prepared after so seeding;

(right upper)
NCD coating after so seeding;

(right down)
B-NCD coating after so seeding

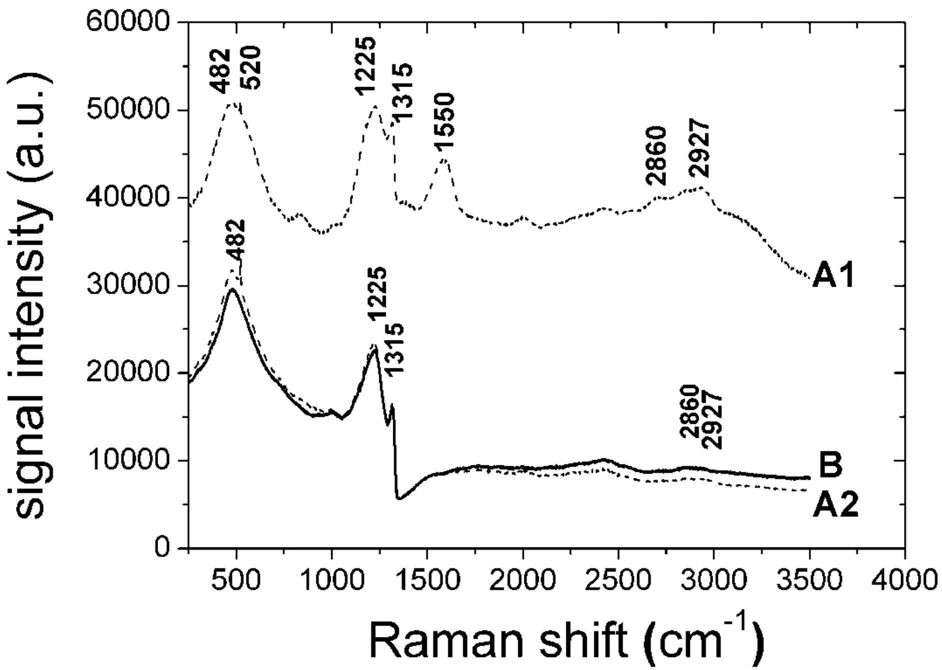
Doping – Raman

Diamond insulator



B/C=0 ppm

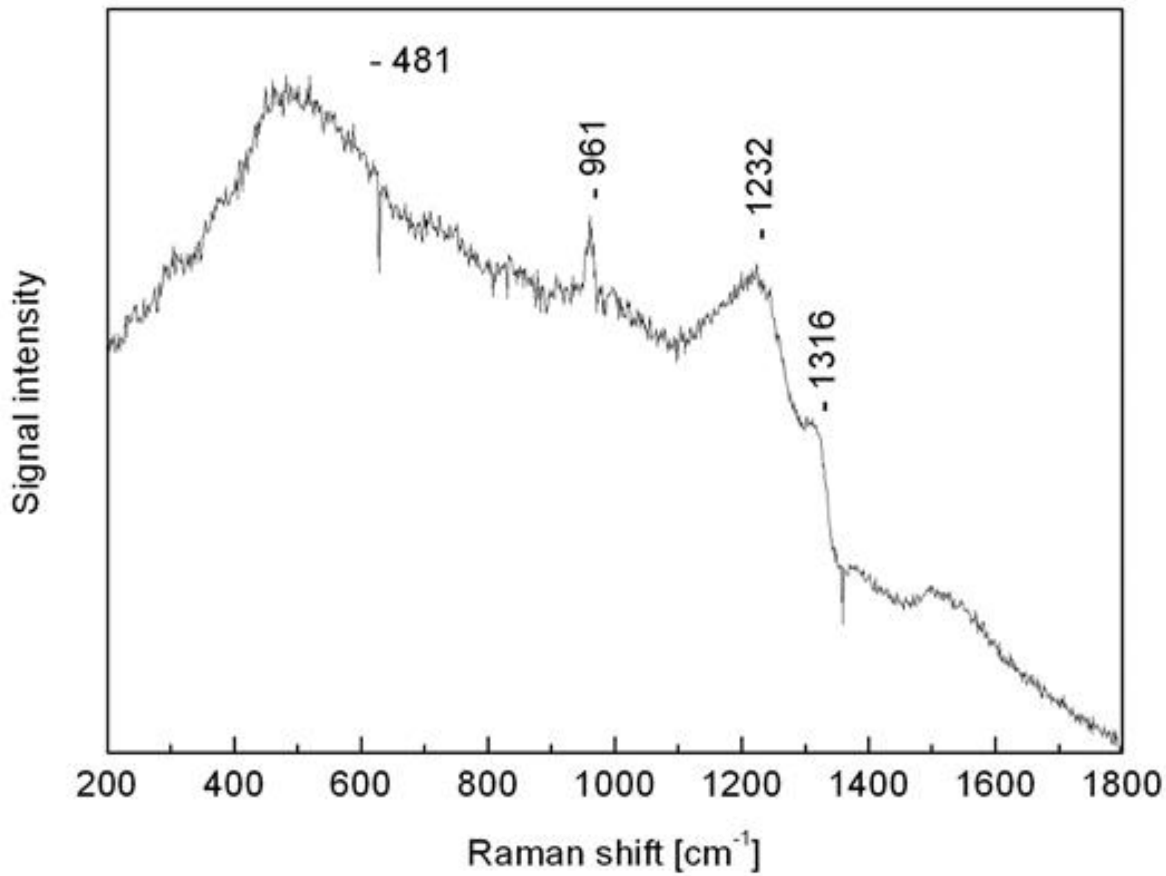
Doped diamond



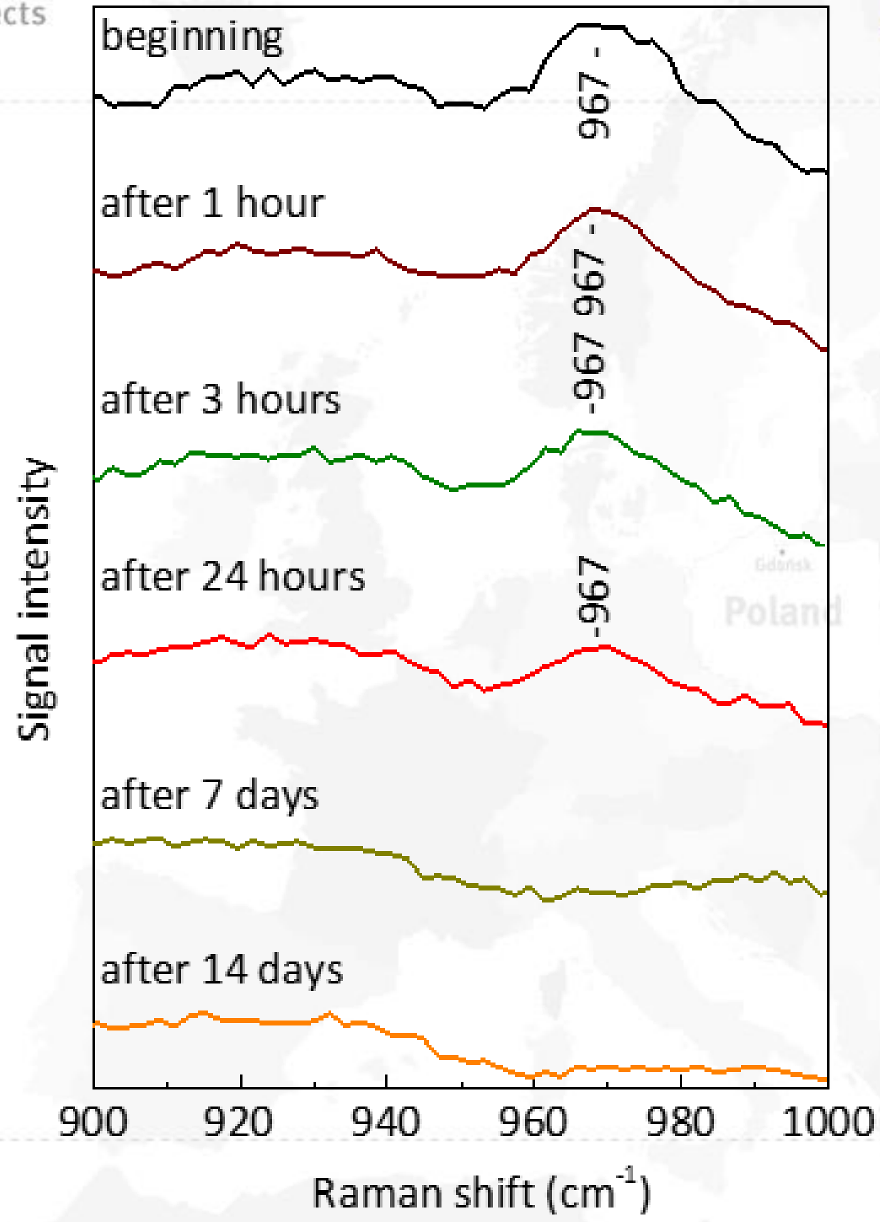
B/C=7000 ppm

Bogdanowicz R, Gnyba M, PSS (A), 2012

Hydroxyapatite layer



Hydroxyapatite in bones



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Conclusions

- Raman and optical microscopy confirmed molecular composition, crystallinity, homogeneity and continuity of undoped and boron doped diamond layers.
- Composition of HAp layer and mineralization of bones/teeth can be investigated
- The method can be used for quality control in manufacturing process.

Acknowledgements

The authors wish to thank Prof. Robert Bogdanowicz, Prof. Andrzej Zieliński, Dr. Michał Sobaszek and Mr. Maciej Głowacki from the Gdańsk University of Technology and Dr. René Beutner and Prof. Dieter Scharnweber for their help in sample preparation.

The financial support from the Gdańsk University of Technology (DS programm) and from the Polish National Centre for Research and Development (NCBiR) under research project No. LIDER/32/205/L-3/11 is gratefully acknowledged.