



SCIENCE
& TECHNOLOGY DAYS
POLAND-EAST



2nd Forum Science & Technology Days Poland-East

22-24.04.2009 Białystok-Białowieża, Poland

ICT ● ECO-ENERGY ● HEALTH ● NMP ● TRANSREGIONAL CO-OPERATION

A New PVD–CVD Method of Deposition DLC Coatings on Medical Implants

Mikalai Chekan



KAPITAŁ LUDZKI
NARODOWA STRATEGIA SPÓJNOŚCI

UNIA EUROPEJSKA
EUROPEJSKI
FUNDUSZ SPOŁECZNY



Projekt współfinansowany przez Unię Europejską w ramach Europejskiego Funduszu Społecznego



A New PVD–CVD Method of Deposition DLC Coatings on Medical Implants

Mikalai Chekan

Vice Head

PLASMOTEG Scientific Engineering Center
Physical Technical Institute
National Academy of Sciences of Belarus

Tel.: +375 17 2118371

Fax: +375 17 2635920

<http://www.plasmoteg.org.by>

E-mail: pec@bas-net.by



Physical Technical Institute

Established: year 1931

Staff: 350 (Researches & Engineers: 208)

Area of Expertise:

- Fundamental and applied researches in the area of developed new composite and special materials and technique of their treatment
- Laser, ion– and electron beam modification of metals in order to tailoring their properties
- Development of vacuum plasma technology of obtaining of thin film materials and super hard coatings for cutting tools and vehicle parts

Last year the institute is determined by Belarusian government as a head enterprise in the area of development of medical devices in the country.



10 Kuprevich St.

Minsk 220141 Belarus

Tel.: +375 17 2118371

Fax: +375 17 2635920

www.phti.belhost.by

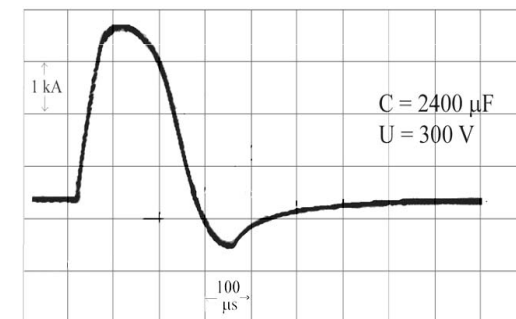
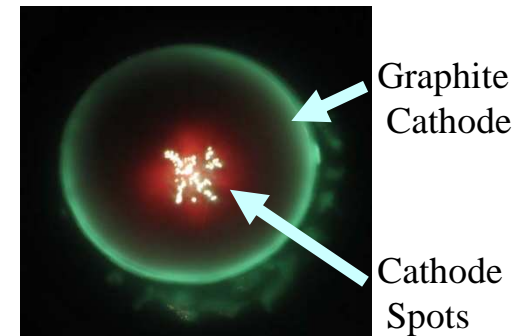
phti@belhost.by



Pulsed arc for DLC film deposition

To deposit thin diamond-like carbon films a pulsed cathodic arc method has been developed. A special plasma source was designed and manufactured.

Carbon plasma is formed in vacuum of $10^{-2} \dots 10^{-3}$ Pa as result of a short-time electrical arc discharge between water cooled graphite cathode and ring-like anode using energy of the capacitor bank magazine.

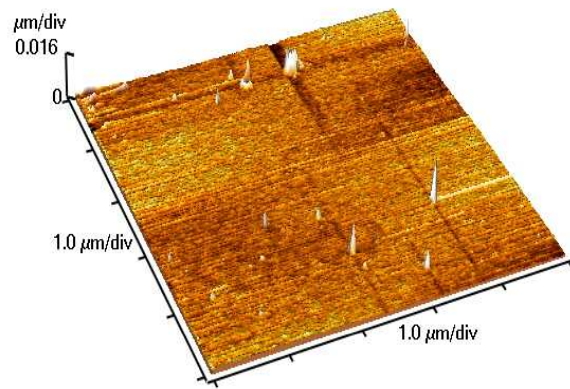


Cathodic spots and current diagram of a pulsed arc discharge: Current maximum is about 3000 A, Pulse duration is about 270 μ s

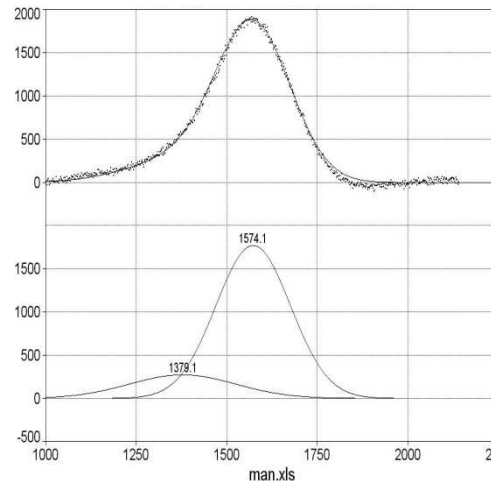




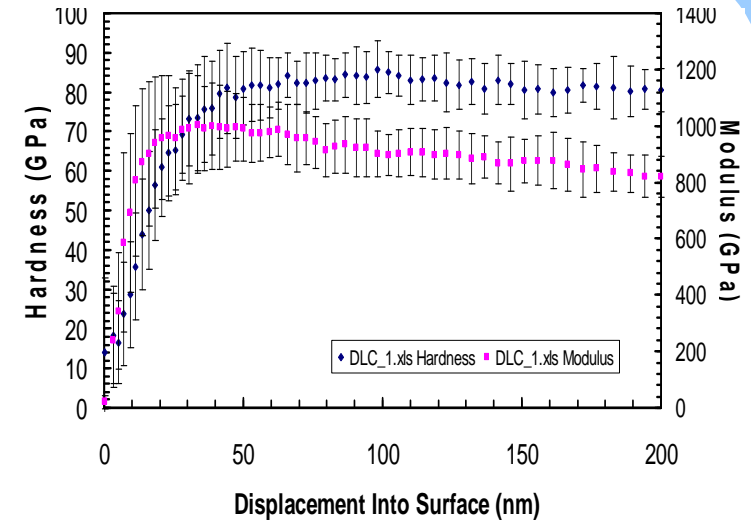
DLC film characterization



AFM image of the DLC film on silicone wafer
 $R_a = 0.19 \text{ nm}$, $R_q = 0.34 \text{ nm}$,
 $R_v-p = 15.96 \text{ nm}$



Raman shift
 D-peak position: 1379.1 cm^{-1}
 G-peak position: 1574.1 cm^{-1}
 $I_D/I_G = 0.15$



Hardness & Young's modulus *vs* nanoindentation depth for the 1200 nm DLC film on the WC substrate
 $H_V = 8500$ (85 GPa), $E = 950 \text{ GPa}$

DLC film specification

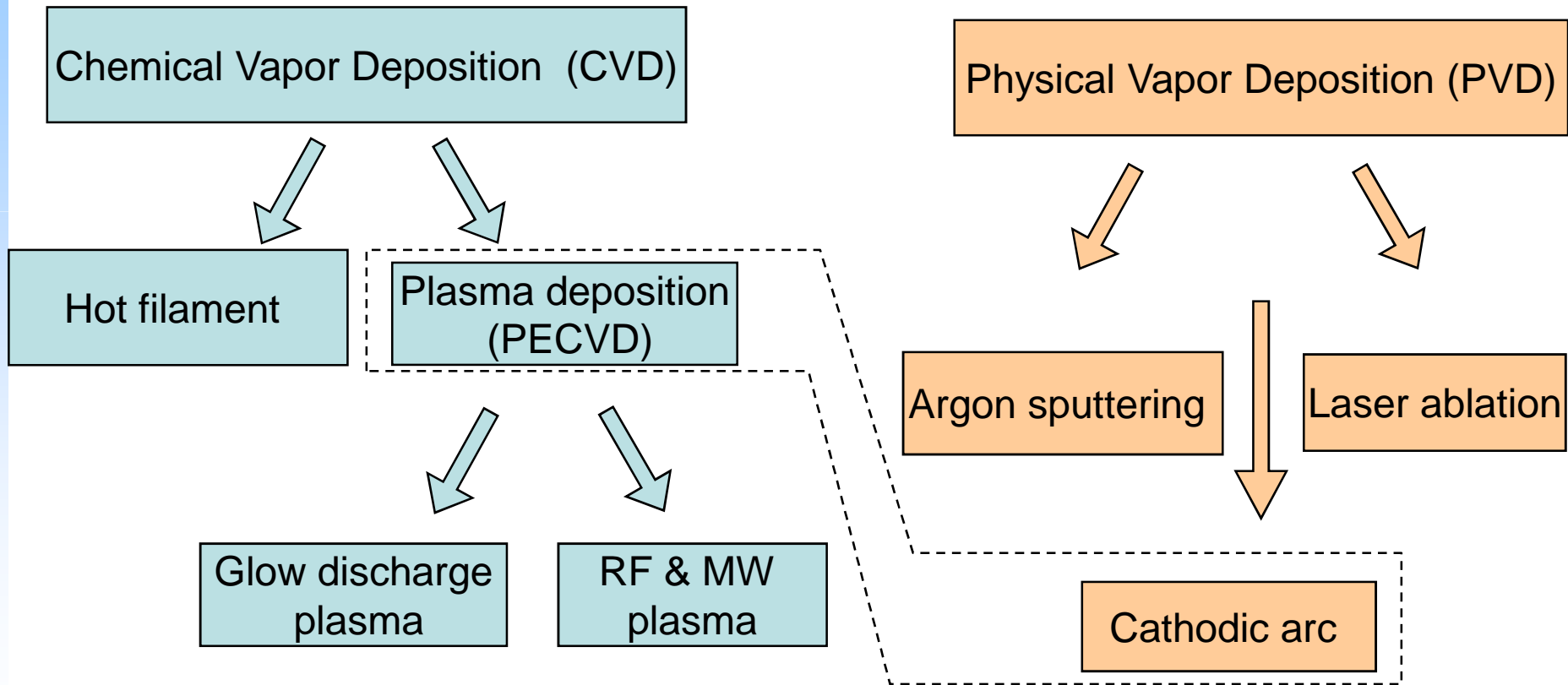
Density, gram/cm^3	2.9...3.2	Thickness, nm	50...200
Hardness, GPa	60...85	Roughness R_a , nm	0.2...0.5
Yung module, GPa	650...950	Friction coefficient	0.05...0.1
Friction coefficient	0.08...0.1	Thermal stability, $^{\circ}\text{C}$	300...350

Problems

- Low deposition rate
- Huge compressive stress
- Low film thickness
- Non-uniform film thickness
- Presence of a lot macroparticles

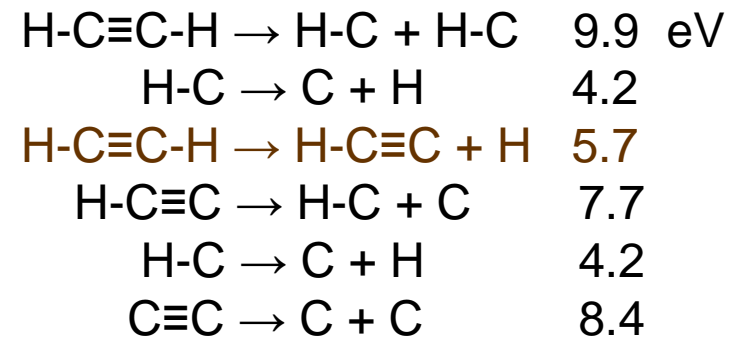
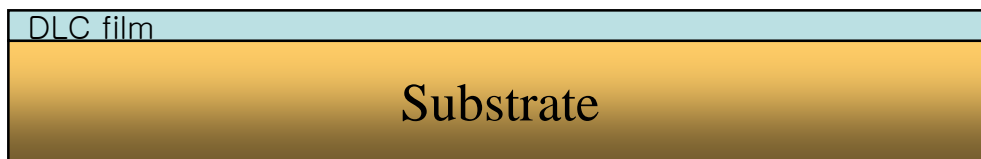
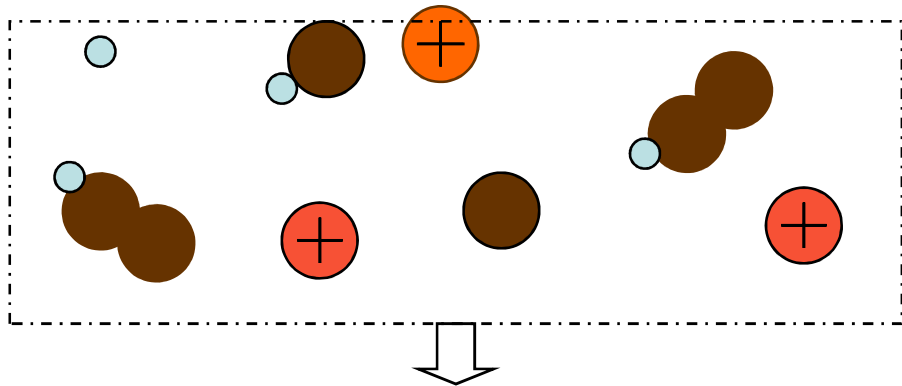
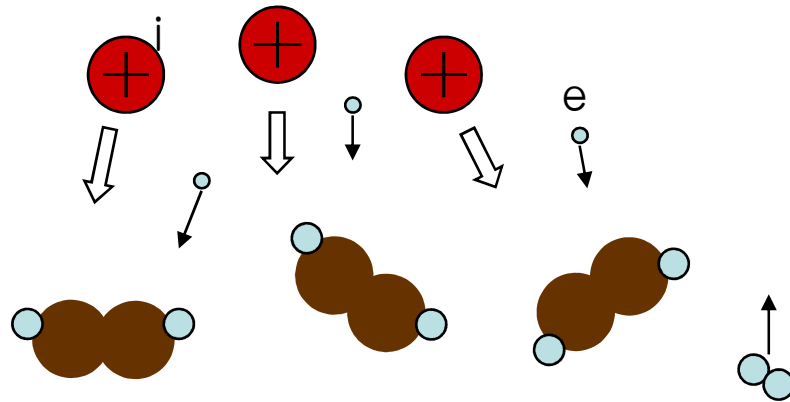


Methods of DLC Film Deposition





Physical & Chemical Processes



Ervin K.M., Gronert S., Barlow S.E. et. Bond Strengths of Ethylene and Acetylene. J. At. Chem. Soc. 1990, V. 112, P. 5750-5759

$$N = \sqrt{2\pi}L(R_c + R_{\text{C}_2\text{H}_2}) P/kT$$

$$R_{\text{C}_2\text{H}_2} = \frac{1}{2}(0.319 + 0.138) \text{ nm}$$

$$L = 30 \text{ cm}, T = 300 \text{ K}$$

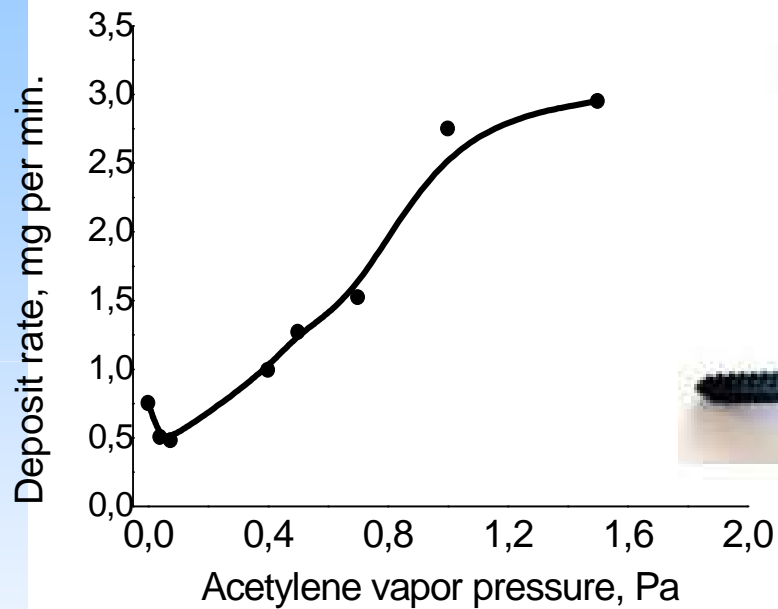
$$N_{\text{max}} = 70 \text{ eV} / 5.7 \text{ eV} \approx 12;$$

$$N_{\text{min}} = 1$$

Conclusion:
Effective acetylene pressure range is from 0.1 Pa to 1 Pa



Deposition Rate & Uniformity of DLC Films



Dependence deposit rate of a DLC film on acetylene vapor pressure



Thin and non-uniform DLC coating



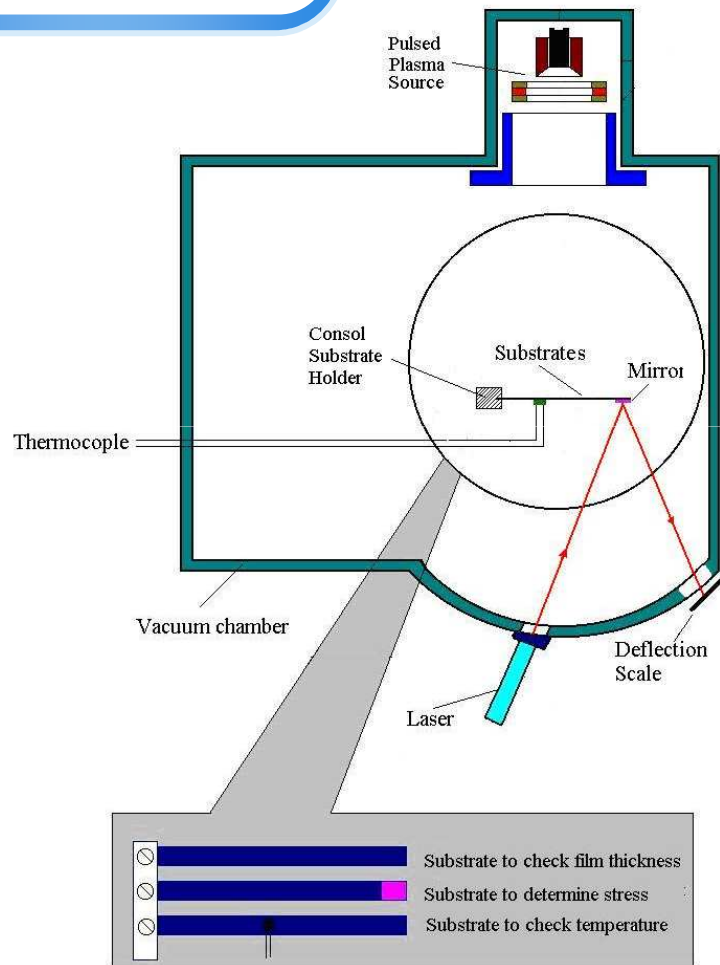
Thick and uniform DLC coating

Conclusion:

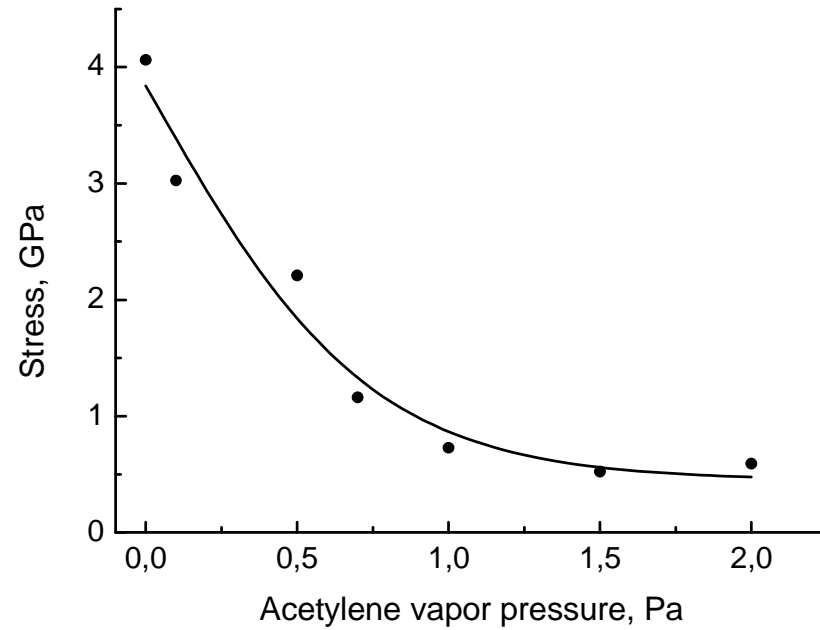
- ✓ Deposit rate in acetylene gas presence increases by a factor of 3 comparing to that in vacuum
- ✓ Uniformity in the film thickness is enhanced from 27% to 60% all over the substrate area of 100 cm²



Intrinsic Stress



Drawing of stress determination *in situ*



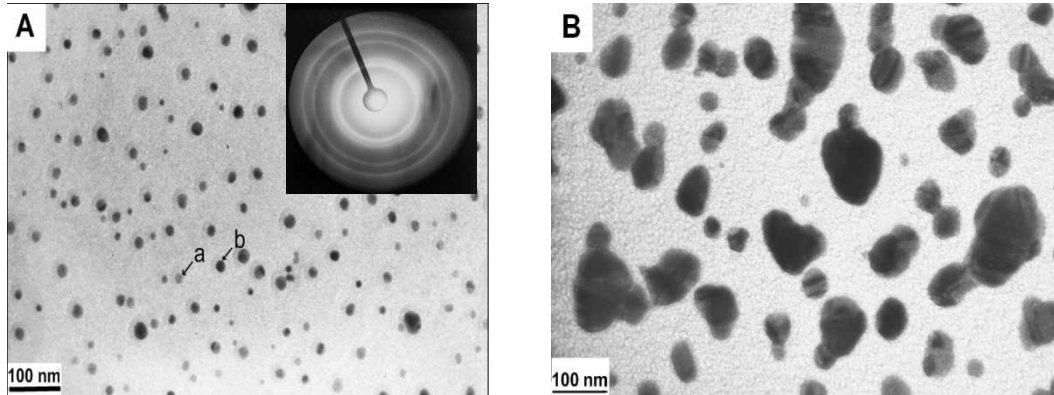
Stress dependence on acetylene pressure

Conclusion:

- ✓ Stress can be reduced in several times by introduction in vacuum chamber acetylene at low pressure



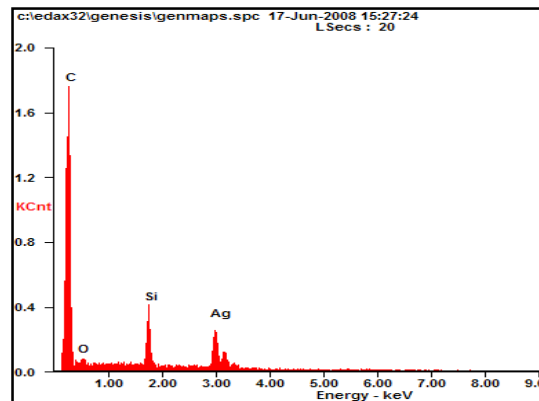
DLC coating characterization



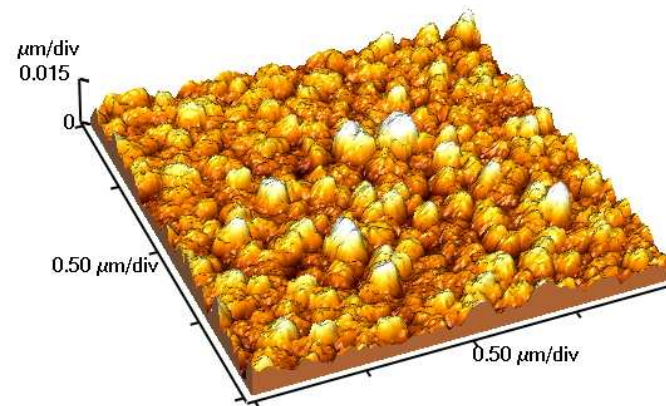
TEM pictures of nanocomposite DLC:Ag film containing silver of (A) 3.5 at.% and (B) 9.0 at.%. Insert is an electron-diffraction pattern.

Table of DLC film element content

<i>Element</i>	<i>Wt%</i>	<i>At%</i>
<i>C</i>	45.05	81.86
<i>O</i>	1.66	02.27
<i>Si</i>	8.87	06.89
<i>Ag</i>	44.42	8.99



Electron microprobe spectrum of DLC:Ag film

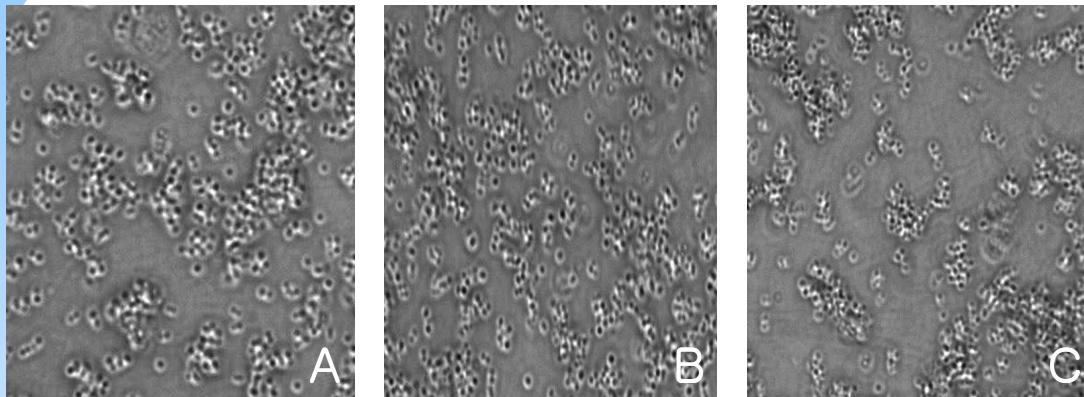


AFM image of DLC:Ag film

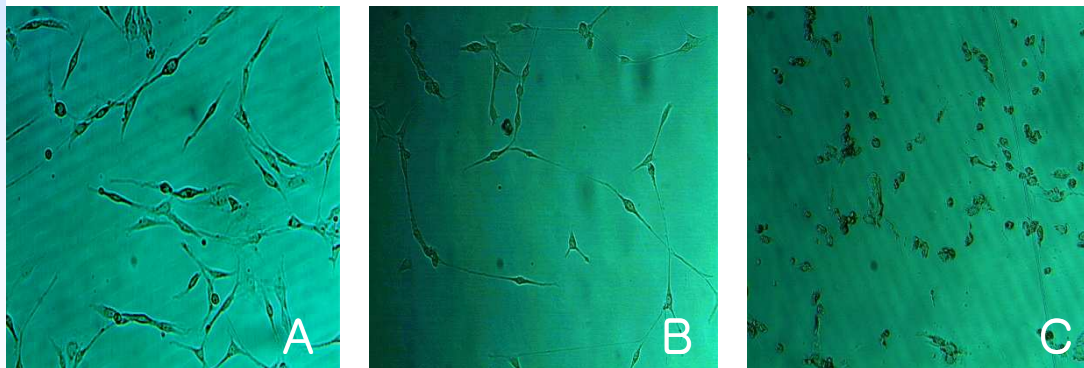
Roughness parameters:
 $R_p-v = 14.52 \text{ nm}$
 $R_q = 1.88 \text{ nm}$
 $R_a = 1.46 \text{ nm}$
 $H_t = 6.09 \text{ nm}$



Biological activity of DLC:Ag films



Bacterium of *Staphylococcus Aureus* on (A) titanium, (B) titanium+ DLC and (C) titanium+ DLC:Ag substrate



Rat Glioma C6 cells placed on (A) titanium, (B) titanium+ DLC, and (C) titanium+ DLC:Ag substrate

Number of bacterium in Goryaev cell (square of 1/400 mm²)

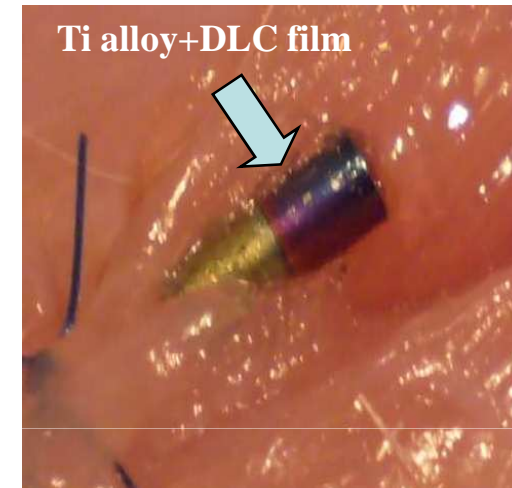
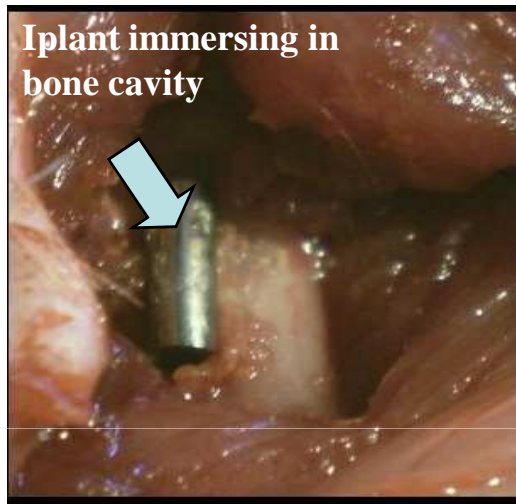
Control	6450
Ti alloy (Al6.8%, V5.3%)	4485
Ti alloy + Ag	4577
Ti alloy / DLC film	4705
Ti alloy / DLC film + Ag	2689

Glioma C6 cells destruction on titanium substrates coated with DLC films

Type of Coating	Destruction, %	
	3 days	5 days
Control	3.4	5.4
Without coating	9.3	33.2
DLC	6.2	39.9
DLC+3.5 at.Ag	11.8	53.7
DLC+6.5 at.%Ag	13.8	66.7



CARBON COATINGS FOR MEDICINE



Kind of coating onto titanium Implant	Number of lab animals (rat)	α 1- Antitripsin (μ mol/litre)	α 2- Macroglobulin (μ mol/litre)
Control	3	4.63	1.42
Without coating	3	1.77	1.26
DLC coating	3	2.95	1.28
DLC:Ag coating	3	3.04	-

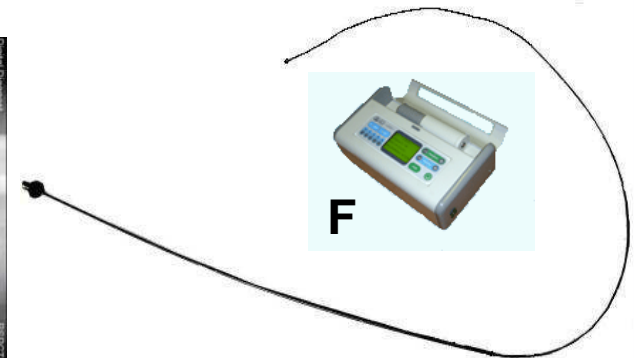
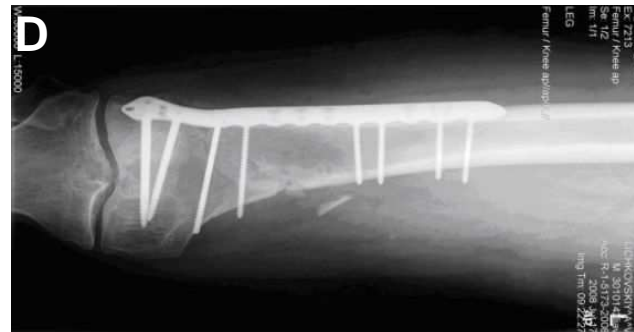
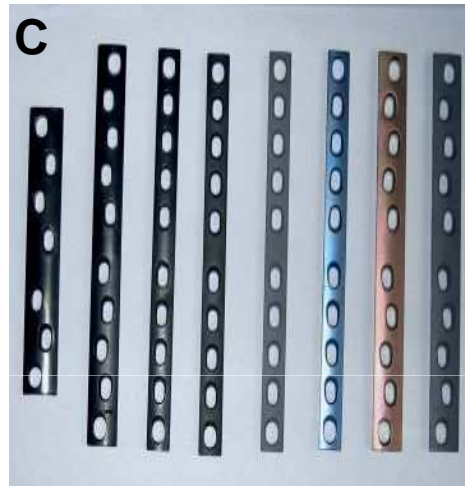
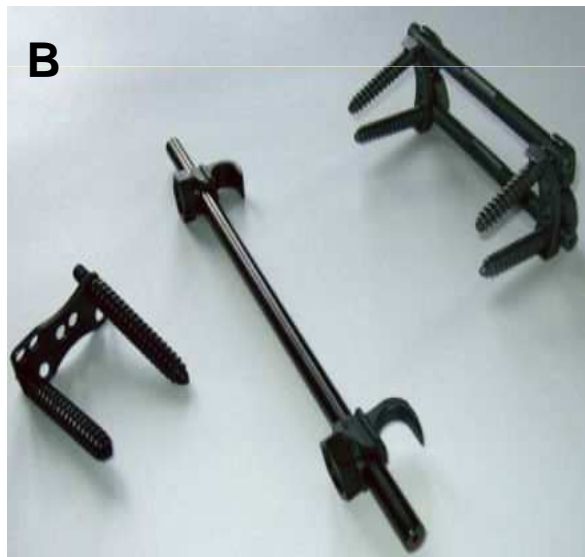
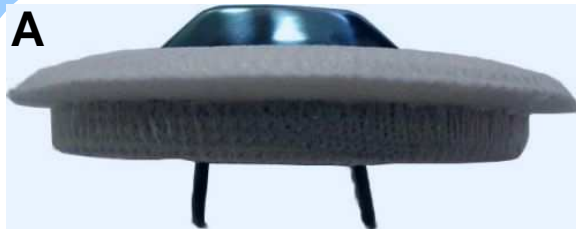
Conclusion

DLC coating:

- ✓ prevents growth of the commissure tissue around the implant surface
- ✓ prevents a large disturb of immune system at implantation
- ✓ nanoparticles of silver reduce of bacteria content almost 2 times



Carbon coating for medical implants



- (A) Artificial head valve, (B) Back bone holder, (C) Titanium plates coated with DLC and TiO_2 , (D) X-ray image of the titanium implant with DLC coating, (E) Rotor of the blood pump for the apparatus of the artificial left ventricle of heart, (F) Ultrasonic waveguide of the thrombus destruction set in human veins



Conclusion

- Pulsed cathodic arc burning in the presence of any hydrocarbon vapor at low pressure provides high deposit rate due to two sources of carbon specimens – cathode spots and decomposed hydrocarbon molecules.
- The combined method gives a possibility to deposit low stressed and high uniformed DLC coatings all over the substrate area.
- Additional arc plasma source is used to dope DLC film with silver in form of nano size disks intercalated in amorphous carbon matrix.
- The nanocomposite DLC:Ag materials possess excellent biocompatible and antibacterial properties as well as prevent tumor cell growth near the implant coated with the composite films.

Collaborate Modes

- ✓ **Research & Development Project**
- ✓ **Equipment & Technology Transfer**
- ✓ **Joint Laboratory**
- ✓ **Intellectual Property Rights Transfer**



We are ready...
and you?



Thanks
for your attention



KAPITAŁ LUDZKI
NARODOWA STRATEGIA SPÓJNOŚCI

UNIA EUROPEJSKA
EUROPEJSKI
FUNDUSZ SPOŁECZNY

