Organic Spintronics

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Conference & Exhibition

High performing DLC coatings by means of Pulsed Plasma Deposition System

Organic Spintronics S.r.l. – BOLOGNA

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Company overview

Established	2003
Location	Via Gobetti 101, Bologna, Italy
Production	Thin film deposition equipments, PPD sources, and laboratory deposition equipments and accessories. Industrial deposition equipments
R&D	Development of novel PPD deposition sources and processes
Vision	Transfer the PPD breakthrough innovation to the industry

Founder: Prof. Carlo Taliani

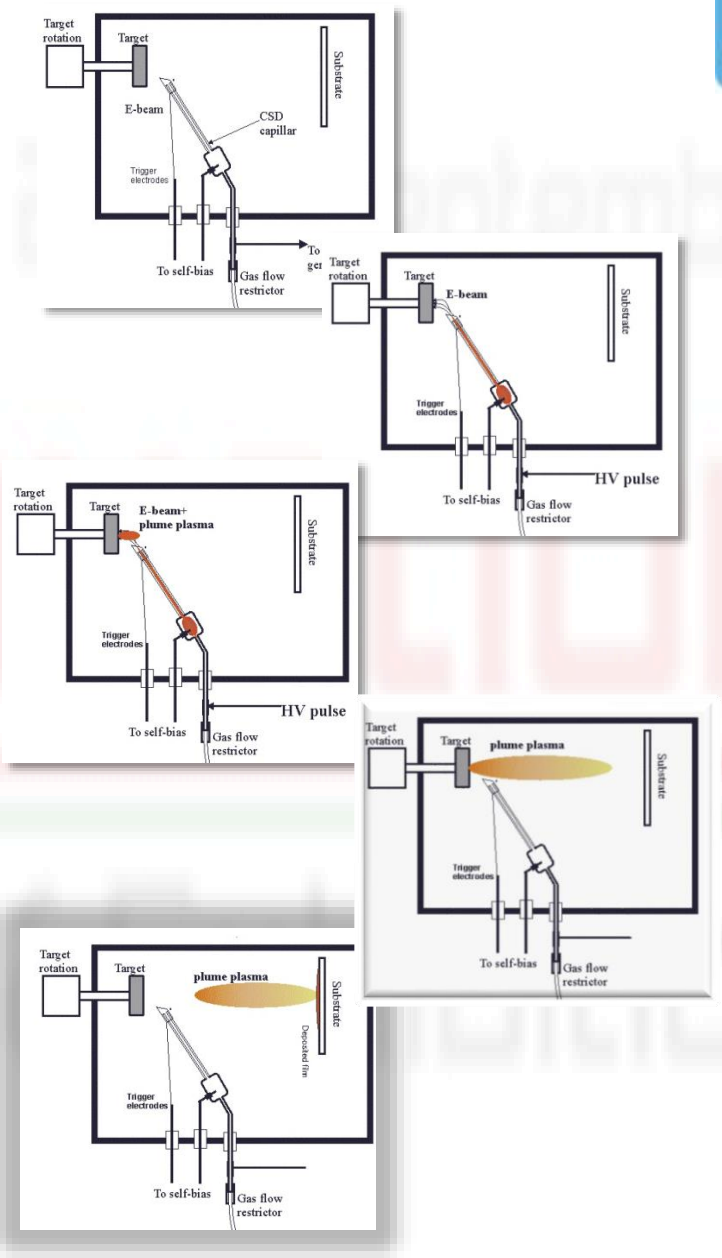
Experience: 40yr+ (1945-2015**)**

- 10100 citations; h index 40 (Thomson Reuter 11/2015)
- **Expertise:** nanoscience, nanotechnology, thin film deposition, organic electronics, spintronics and hybrid electronics

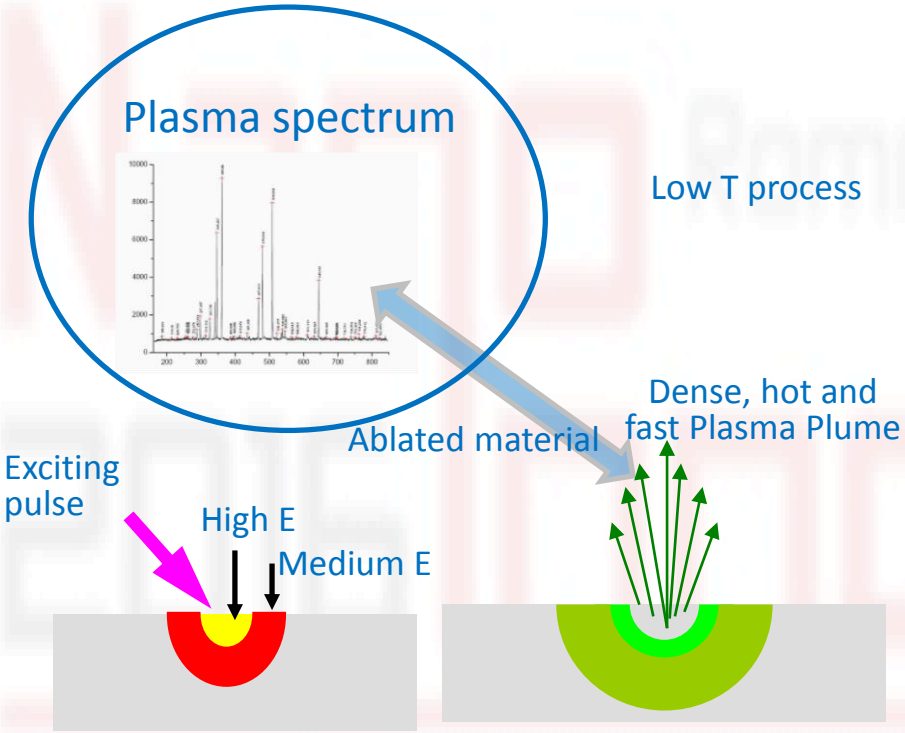
Organic Spintronics takes advantage of the scientific and technical **excellence** of the **Bologna CNR Area** and it is connected with many **High Technology Technopoles** of ER region.

PPD Working Principle and advantages:

- High-voltage difference (up to 20kV) and high energy density start the electron beam to ablate the target.
- High current density (up to 20 KA/cm^2) and gas generate a dense (up to 10^{17} cm^{-3}) and highly ionized plume.
- The plume propagates toward the substrate. The plasma density decreases with the distance (<10^{14} cm^{-3} at few cm distance) from the target. The plasma species are ballistic.
- The thin film is formed once the plume species impact on the substrate.
- Because of the high energy of the plume together with its high ionicity, a crystalline film is obtained.



PPD Working Principle: the ablation



Ablation process performed onto target surface, ejects a fast, dense and fully ionized plasma which spread normal to the target surface forming a film on a substrate.

Ablation forms a plasma plume

- High kinetic energy
- High electronic energy
- **Any material can be deposited by the electron-matter interaction**
- **Almost any gas can be used as working gas**

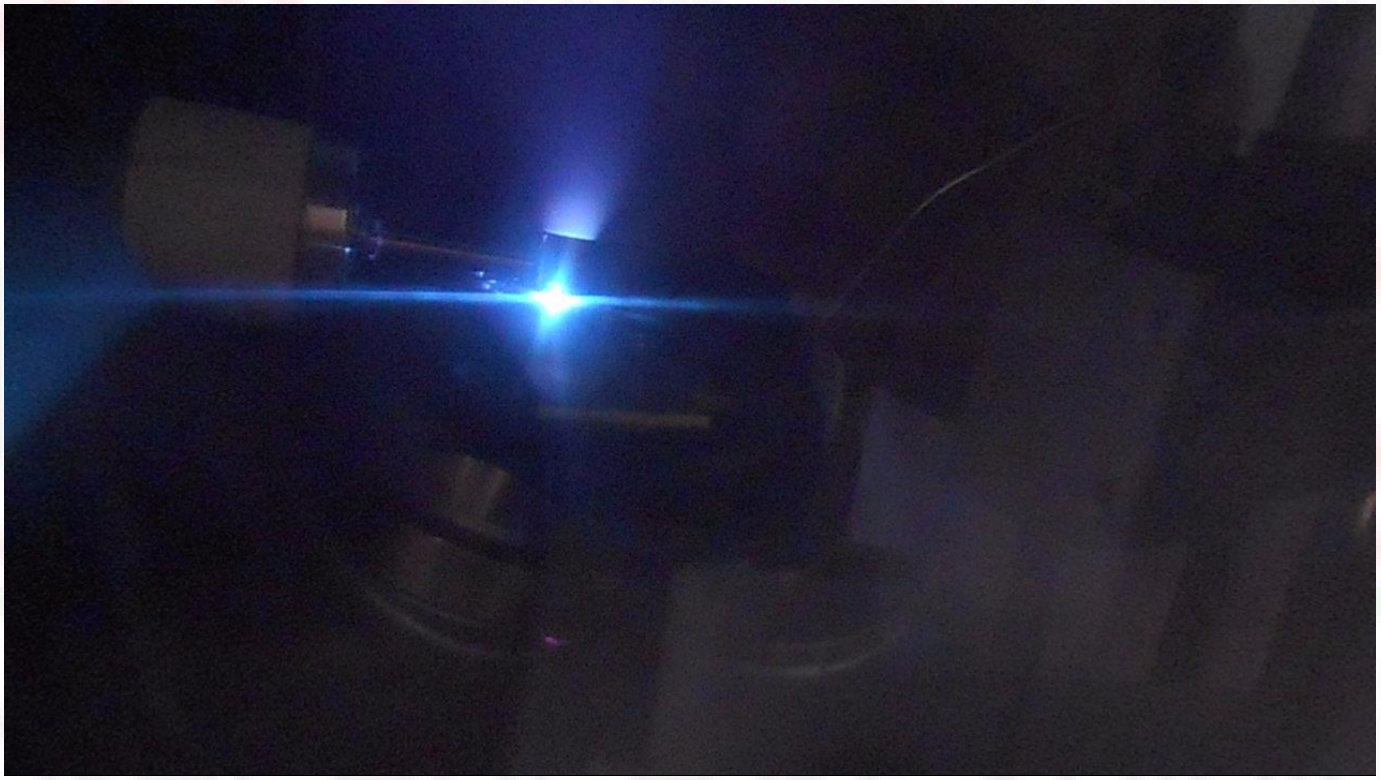
Microsecond pulse duration

- Gaussian deposition profile
- **Room temperature deposition**
- No damage to plastic substrates

PPD advantages

- High deposition rate (up to 200 Hz)
- Composition transfer
- Scaling the area up to industrial needs
- High power efficiency

PPD GEN V Source “live in action”



PPD Technological Roadmap





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For R&D

- 2003 - PPD Gen I @ 2 Hz, 5 nm/min
- 2004 - PPD Gen II @ 10 Hz, 10 nm/min
- 2006 - PPD Gen III @ 20 Hz, 20-30 nm/min
- 2009 - PPD Gen III Twin Spark (one or two targets)
- 2011 - PPD Gen IV @ 100 Hz, up to 200 nm/min
- 2011 - PPD Gen IV Twin Spark
- 2013 - Mixing material from different targets with Twin Spark

For Industrial Production

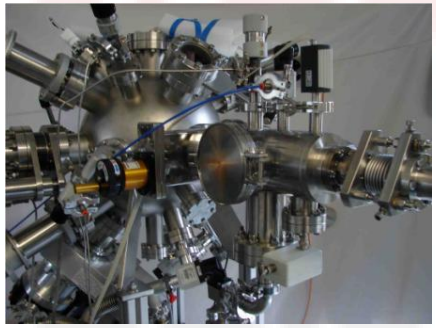
- 2006 - PPD linear deposition demonstration
- 2012 – PPD Gen IV - PRO R&D, new focusing
- 2013 - PPD GEN IV CW linear Industrial prototype module
- 2015 - PPD GEN V @ 200 Hz, up to 500 nm/min

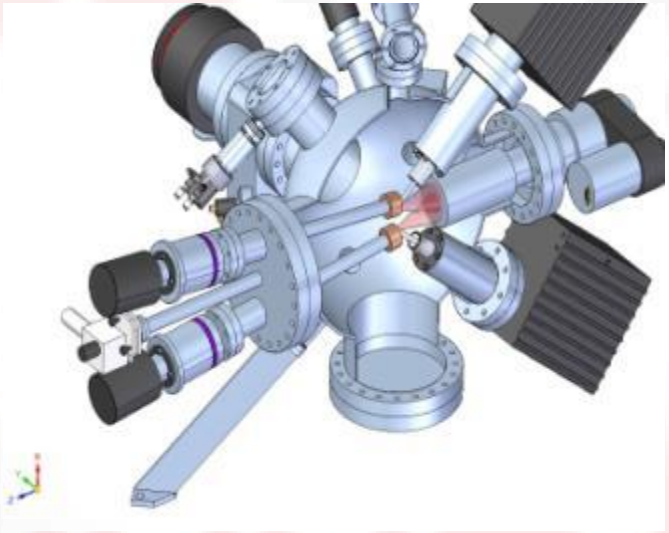




PPD Twin Spark system for R&D

Up to 3” diameter deposition / co-deposition



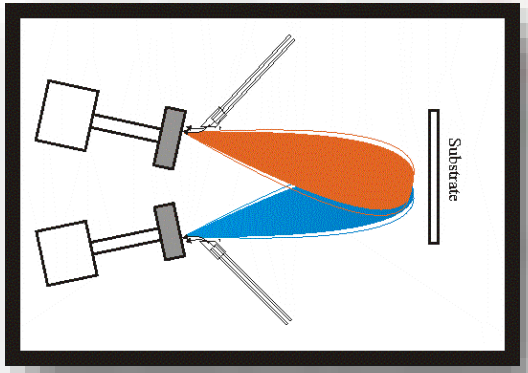


2 – 3 “ PPD deposition system

- 350 mm diam. UHV chamber
- Load – lock (LL)
- RF cleaning in LL
- In-situ laser thickness monitor and control
- **5 % thickness homogeneity at 3 sigma**

Two PPD sources

- For wider area
- For co-deposition
- For **unconventional doping by plume mixing**



- Control of each plume timing, intensity, temperature
- Combine the composition of complex targets material in the deposited film
- Control the relative amount of material from each target to obtain out-of-equilibrium composition of the film (such as magnetic doping, p-doping, etc)
- Control delay of the plumes arriving to the substrate

DLC based treatments

sp^2 and sp^3 carbon bonds in diamond like carbon (DLC) films

- sp^2 gives rise to a planar (graphitic) network
- sp^3 forms a tridimensional (diamond) network.
- sp^3 / sp^2 and the distribution of the relative clusters produce materials with different properties.
- Hardness depends on sp^3 / sp^2 varying from 10 to 80 GPa
- The hardest form is **ta-C**, i.e. tetrahedral DLC, showing an **sp^3 percentage above 40 – 80 %.** (Hydrogen free.)
- Relevant characteristics for the application in mechanics are hardness , smoothness, low friction and high adhesion to the substrate

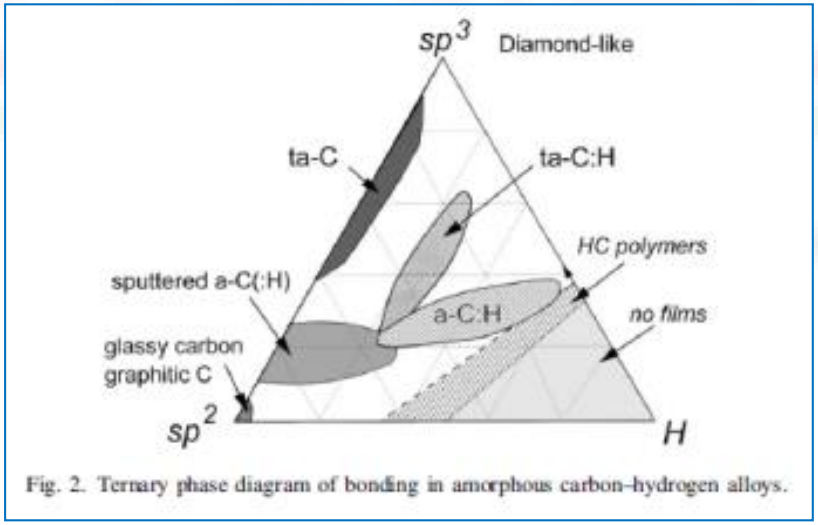


Fig. 2. Ternary phase diagram of bonding in amorphous carbon–hydrogen alloys.

Technologies for DLC surface treatments

Fabrication technology	Achronim	Hardness (Gpa)	Fiction C
Hybrid sputtering and CVD	PVD/PACVD	8 - 22	0,1 -0,2
Plasma assisted chemical vapor deposition	PACVD	15-35	0,05 - 0,15
Unbalanced magnetron sputtering	PVD	20-40	0,05 - 0,1
Filtered cathodic vacuum arc deposition	FCVA	30-70	0,02 - 0,1
Pulsed laser deposition	PLD	30-80	0,02 - 0,1

DLC made by PPD: OUR RESULTS

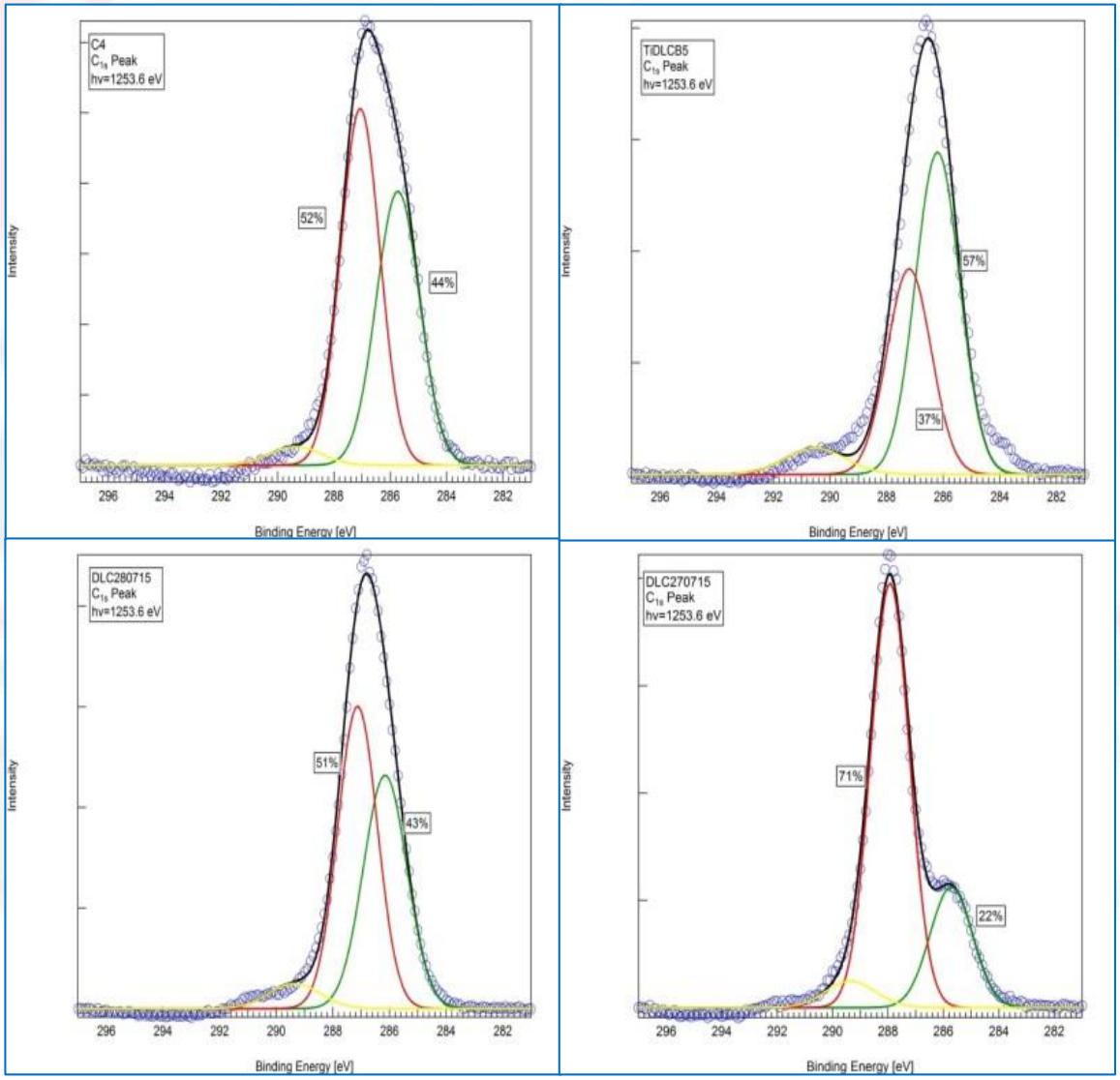
PPD Parameters:

- Voltage
- Frequency
- Target-substrate distance
- Working Gas Pressure

Property	Characterization
• High sp^3/sp^2 ratio	• XPS Results
• High hardness	• Nano – Indentation
• Low roughness	• AFM / SEM analysis
• High adhesion	• Scratch Tests /SEM

PPD DLC Depositions – Property: sp^3 content

XPS Results : sp^3 / sp^2 in collaboration with: CNR - ISOF



experimental curve

sp^3 curve

sp^2 curve

Sample	% sp^3	% sp^2
DLCC4	52	44
DLCB5	37	57
DLCC5	51	43
DLCC6	71	22

PPD DLC Depositions – Property: Hardness

Nano-Indentation Test Results: Hardness and Elastic Modulus

in collaboration with University of Modena

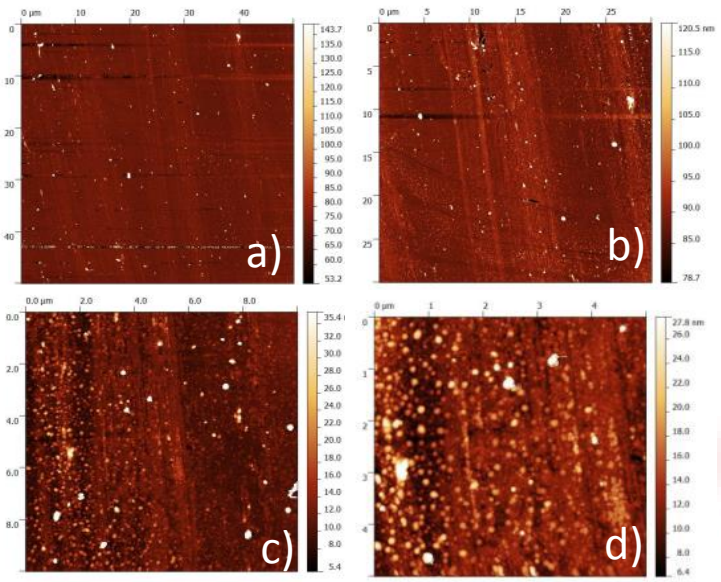
Sample	H (GPa)	E (GPa)
DLC09_01	21.6±2.1	292±130
DLC15_01	26.2±3.6	380±85
DLC31_01	33.8±1.8	434±110

WC polished substrates

Parametri di prova per Nano indentation test (cella da 1 mN)

Carico di contatto (mN) = 0.05
Carico Finale (mN) = 1
Loading rate (mN/mm) = 2
Approach Speed (micron/min) = 2
Creep (s) = 10
Geometria dell'indenter: Berkovich
Materiale dell'indenter (tip): Diamante

PPD DLC Depositions – Property: low friction surface



AFM Results : roughness

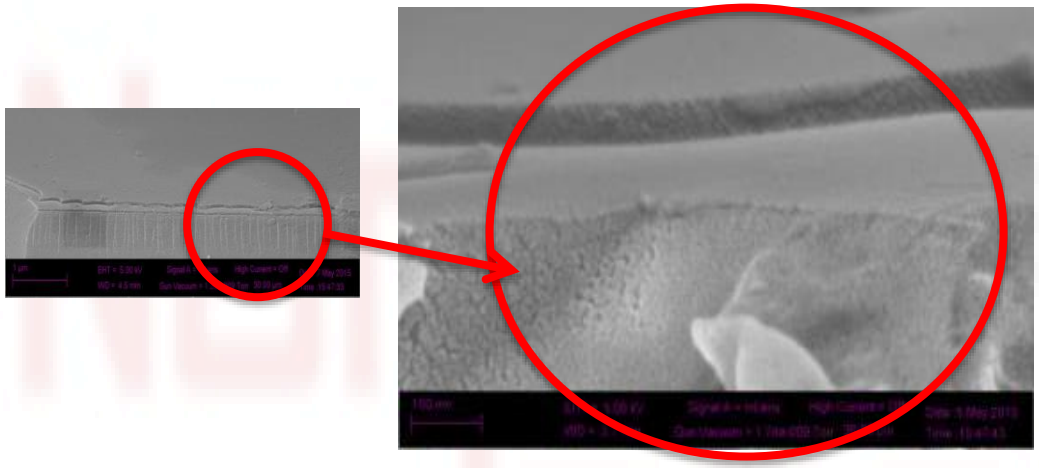
in collaboration with: CNR - ISMN

	Area (nmxnm)	Roughness (nm)	S D (nm)
a)	50x50	6.0	4.6
b)	30x30	4.6	3.2
c)	10x10	4.6	3.4
d)	5x5	3.6	2.2

SEM Results: smoothness

in collaboration with: CNR - IMM

PPD DLC Depositions – Property: adhesion to substrate



SEM Results: adhesion layer

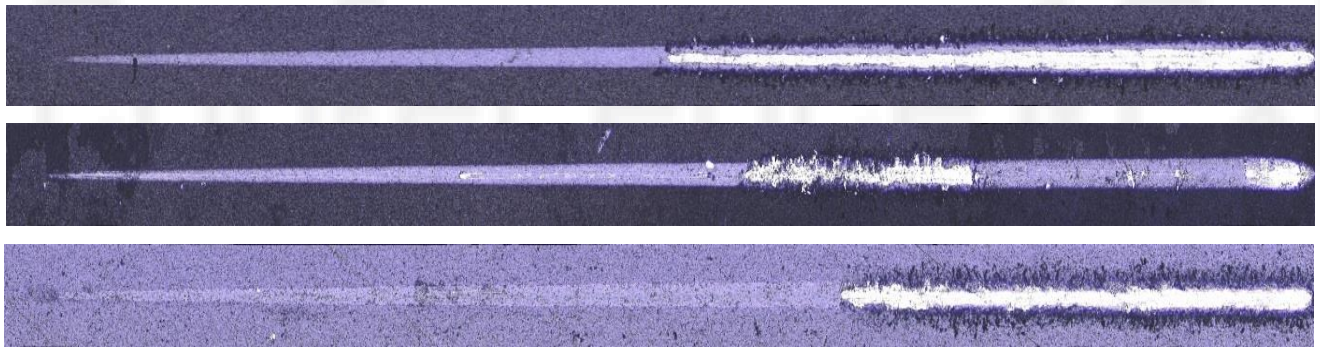
in collaboration with: CNR - IMM

Scratch Tests: DLC film adhesion

in collaboration with: University of Modena

Sample	Delamination Force (mN)
DLC 29_01	5200 ± 350
DLC26_01	7100 ± 450
DLC14_01	9400 ± 640

DLC thin film was very compact: internal planes showed an extremely high adhesion between themselves. In fact only total delamination strength can be evaluated.



Parametri di prova per Scratch Test

Velocità di Traslazione (mm/min) = 1
Velocità di Applicazione carico (N/min) = 5
Carico Iniziale (mN) = 10
Carico Massimo (N) = 30
Tipologia di Indenter : Rockwell
Dimensioni della punta: 200 micron

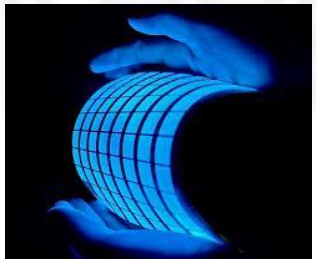
Today Applications

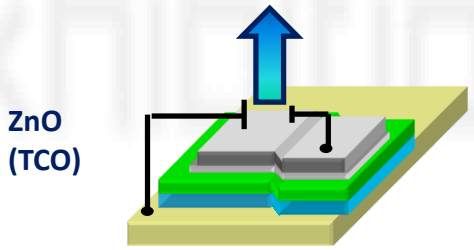
Bio-compatible coating

- More than 600 000 knee replacements are performed each year worldwide using a plastic spacer between two metallic parts.
- The plastic spacer provides the smooth movement and minimal wear of the articulation, it is prone to degrade in 10-15 years
- An hard coating on the plastic spacer can assure a longer lifetime
- PPD system allows to protect plastic spacer with different several biocompatible materials: TiOx; ZrOx; DLC; Phosphates

Transparent Conductive Oxide TCO

- TCO are an essential part of the display, OLED and solar panels industries.
- In_2O_3, ZnO are TCO common materials.
- PPD deposition allow to deposit on materials with an high temperature sensitivity.
- OS developed the processes for TCO fabrication for new generation of **flexible plastic displays** and solar cells





Materials and technology for tomorrow

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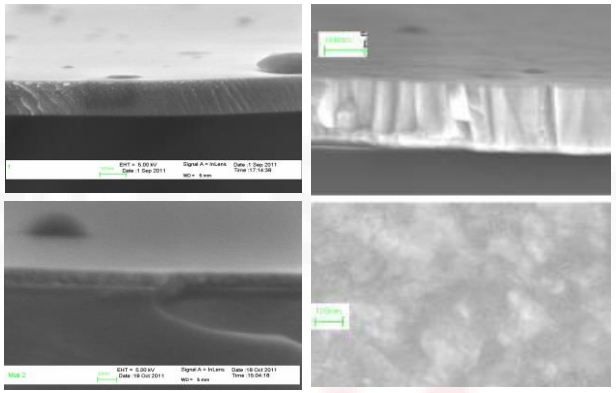
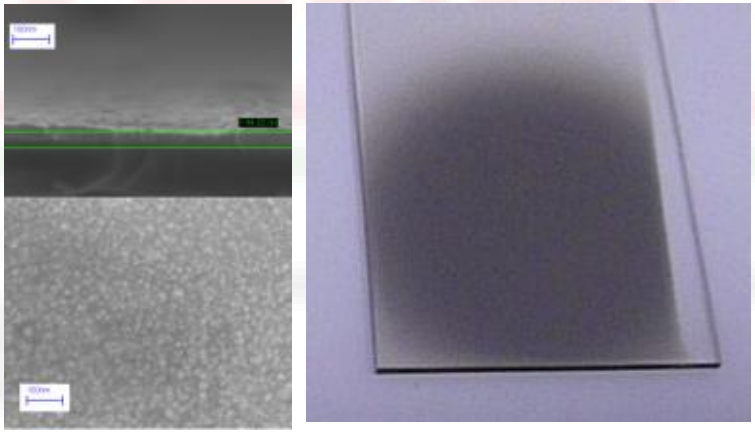
High Performance materials applications

- ✓ High melting point materials: Ta (3014°C) , W (3422°C), Mo (2626°C)
- ✓ Highly conductive materials: Al, Cu
- ✓ High dielectric constant and High gap materials (up to 500) : BST, GaN
- ✓ Decorative coatings: CeOx, TiOx, DLC
- ✓ Very soft materials: Teflon, Tin
- ✓ Materials and Semiconductors for Electronic Device: GaN; BST; ZnO-P; etc.
- ✓ Materials for Batteries: Compounds of Lithium and Phosphate



SEM of Tantalum, Molybdenum and Tungsten films



Images of Copper and Aluminium films

Intellectual property protection: OS's Patent Portfolio

EP 1 867 221 - Apparatus PPD Source Gen III

WO2010IB00644 - PPD Source Gen IV

WO2011IT00301 - PPD Source Gen IV

WO2014097262 - PPD Source Gen V

ITMI20061185 – Deposition of Metal Conductive Oxide

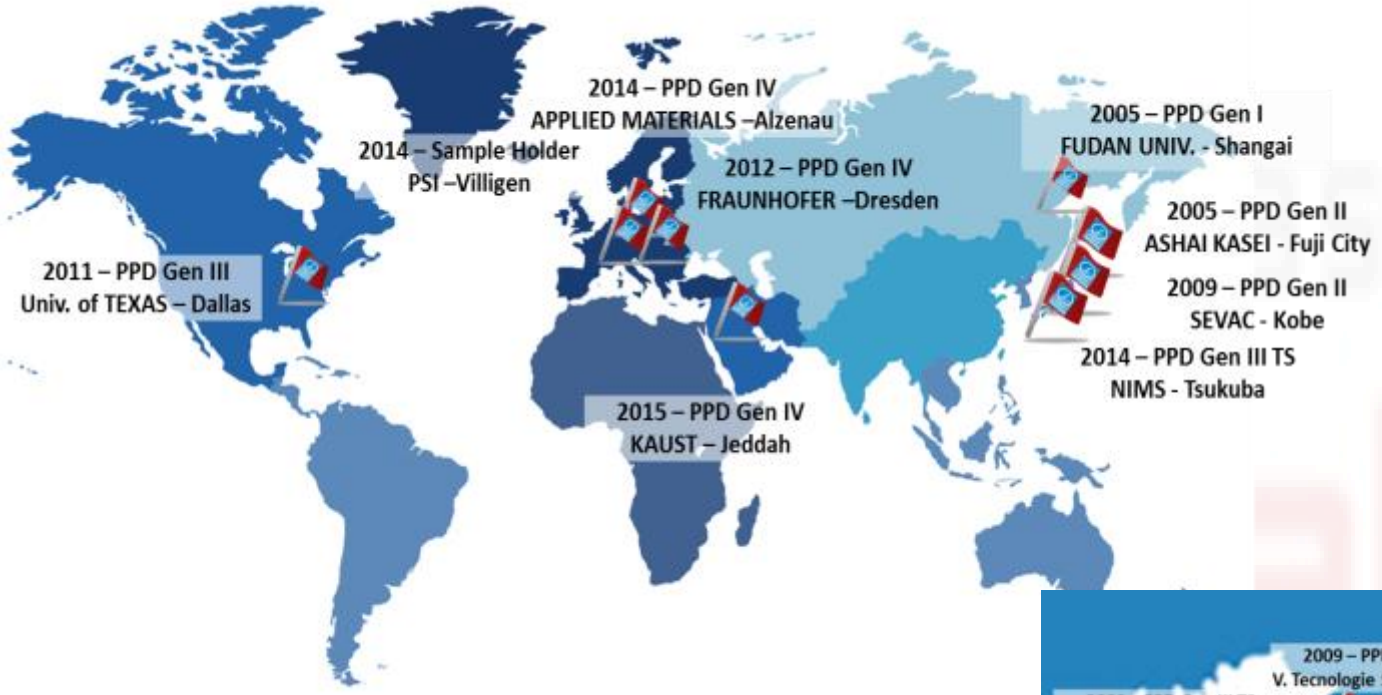
WO2007EP64158 - Transparent Conductive Oxides

ITBO20100568 – High Dielectric Constant Material

WO2011148251- Technology for making Solar Cells

WO2011IB54182 - Bio-compatible materials

OS' PPD Installations World Wide



OS is pleased to announce a

special sales promotion

of its

PPD Basic System equipped with one Source

until December 31st 2016

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Thanks for your attention