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The deposition of hard, transparent, wear resistant, DLC coatings using magnetron sputtering

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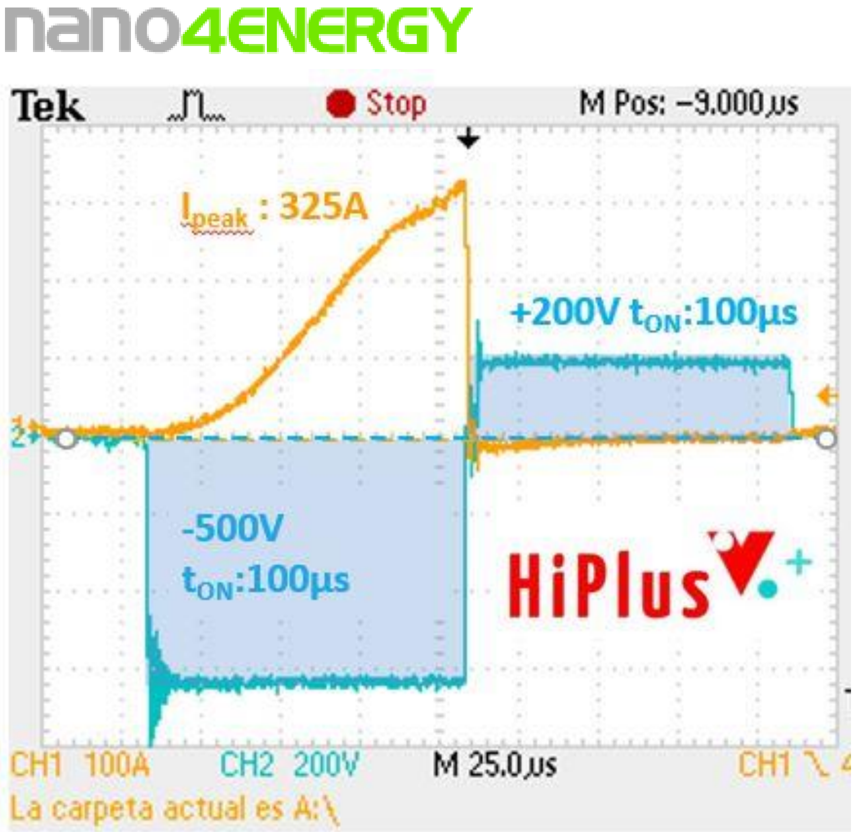
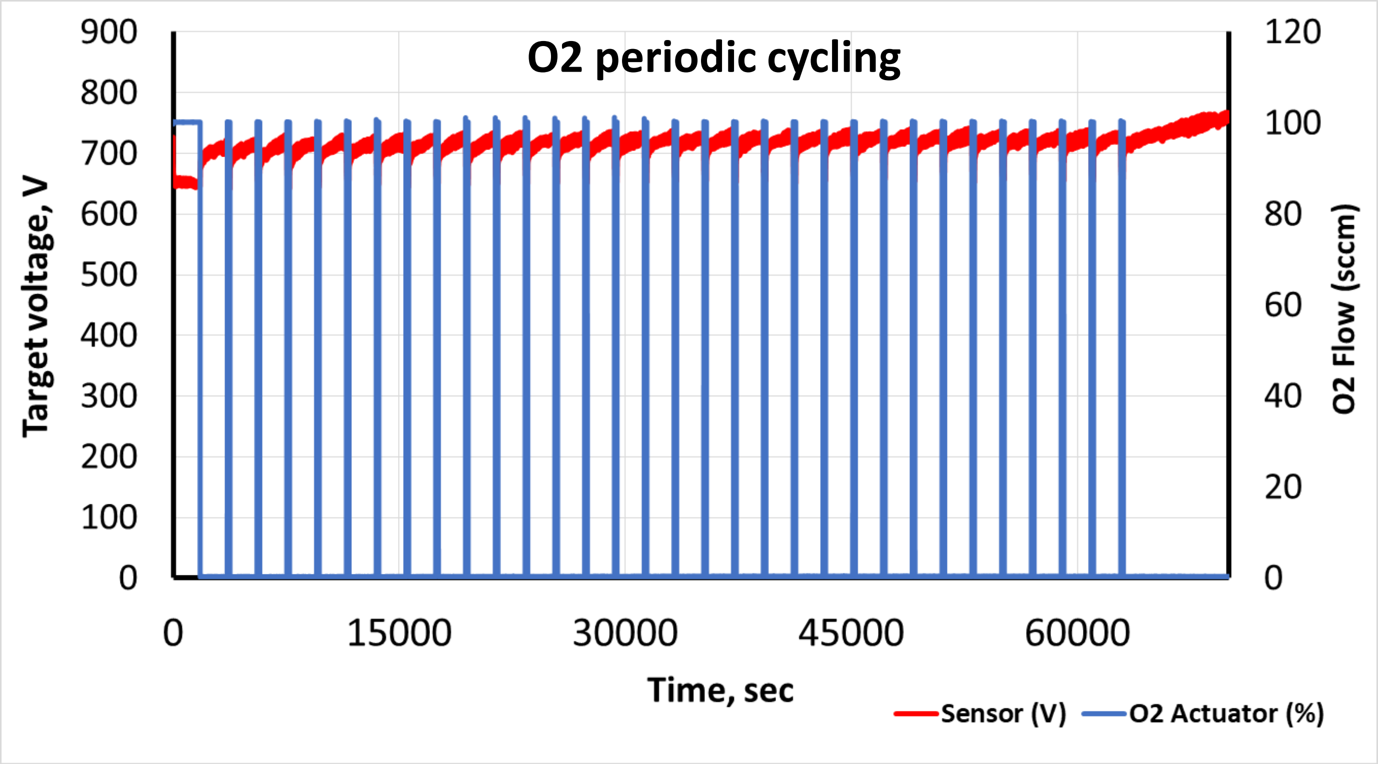
Transparent Carbon coating development with Nano4Energy

- A series of patents have been issued (since 2017) for hard Carbon deposition on glass and long process stability





Outline

❑ 1) Introduction to DLC

- What is DLC
- Magnetron sputtering for DLC
- Hydrogen and ion bombardment

❑ 2) Gencoa's GRS-C Rotatable Magnetron Vacuum System

- Optix remote plasma sensing of H
- Active Anode – enhancing ion energy
- Target voltage stability with O2 cycling

❑ 3) Gencoa DLC on glass

- Optical properties
- Tribo. performance under low loads

❑ 4) Gencoa DLC and Hard Transparent Underlayer

- Tribo. performance under high loads
- Hardness and scratch resistance

I - DLC Production Methods

Diamond Like Carbon (DLC) has wide range of applications due to favourable chemical and physical properties, with different approaches used for the fabrication of DLC thin films

❑ Chemical vapour deposition

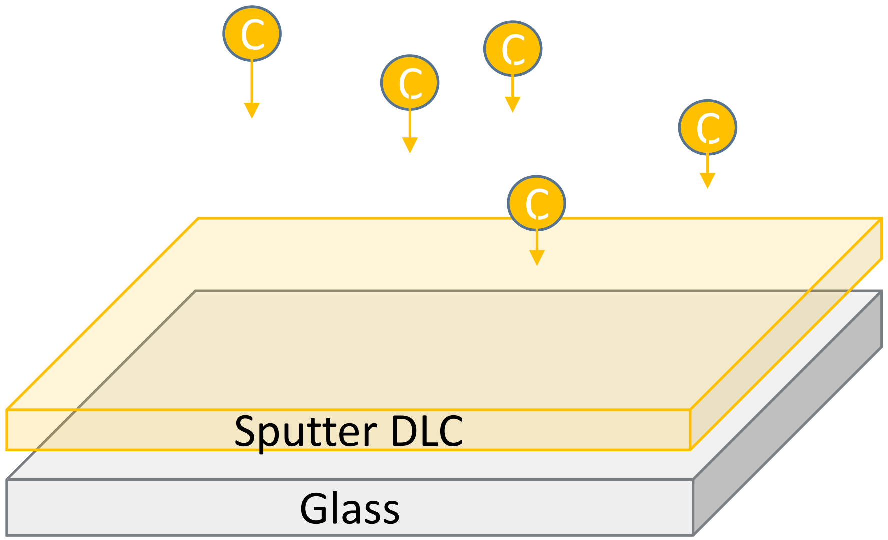
- Plasma enhanced

❑ **Physical vapour deposition**

- **Magnetron Sputtering (MS)**

Gencoa specialise in a form of **MS** to produce hard transparent DLC

- Dual Rotatable Electrode (GRS-C)
- AC MF, Square Wave, HiPIMS



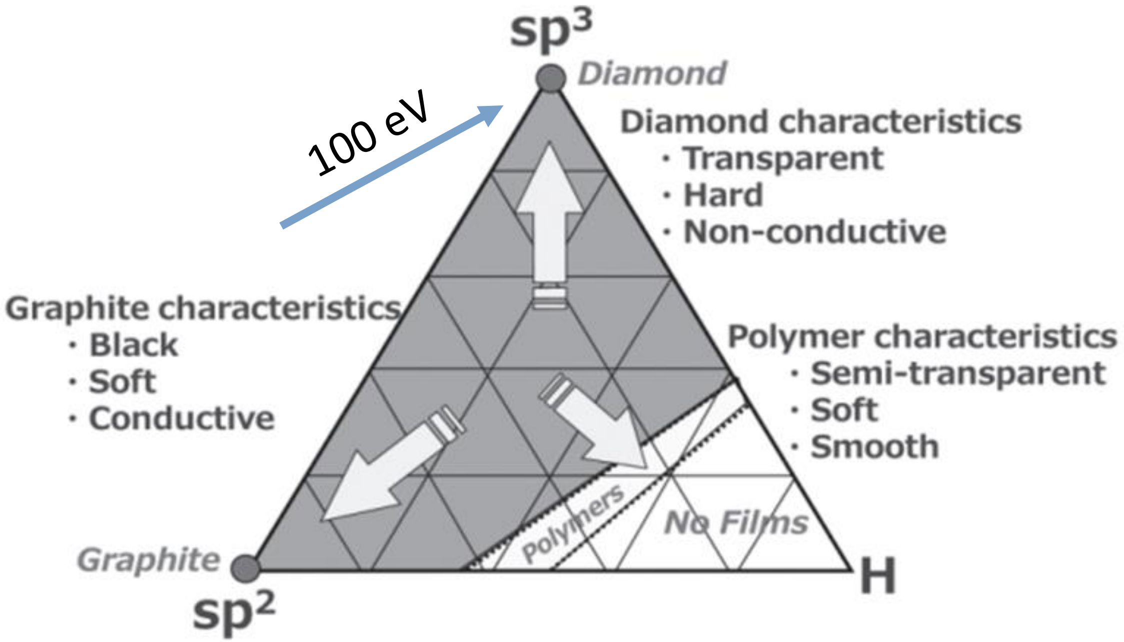
I - DLC Production: Magnetron Sputtering

The unique properties of DLC layers are largely governed by two parameters:

1) Its bonding configuration (the sp^3/sp^2 ratio)

2) The hydrogen content within the DLC layer.

To attain hard, transparent DLC coatings (high sp3 and sufficient H) we can approach the issue in two ways



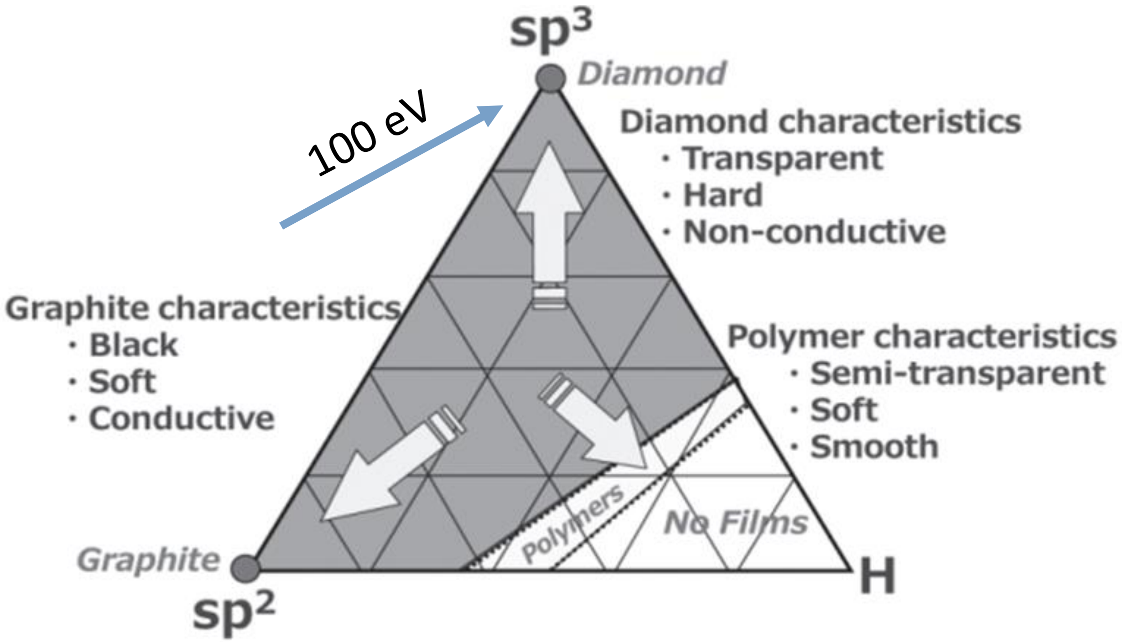
I - DLC Production: Magnetron Sputtering

✓ **Manipulate the plasma surface interaction**

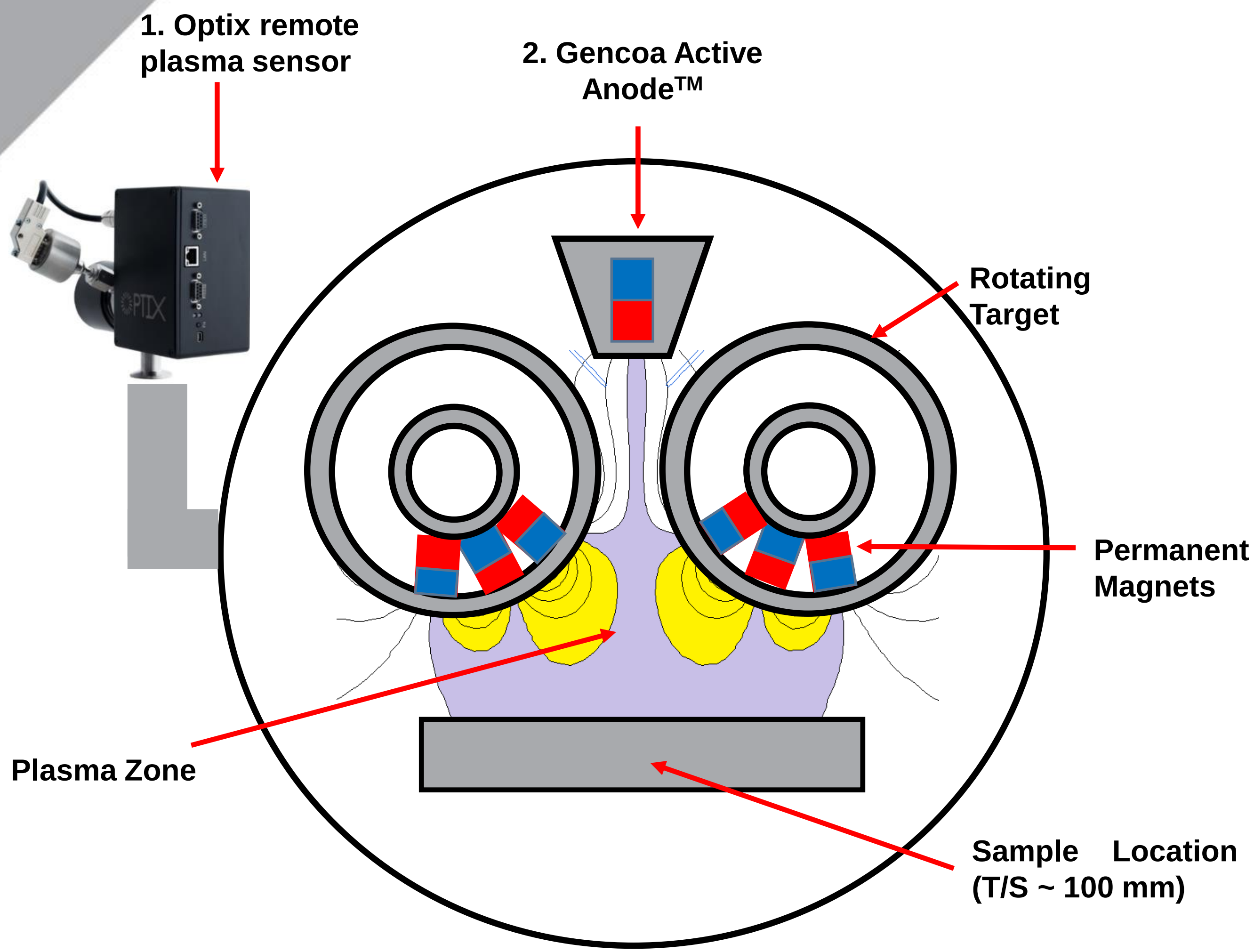
- Boost energy of sputter gas (Ar, O2)

✓ **Assess H content in the DLC layer**

- Vacuum condition



II - Gencoa GRS-C Rotatable Magnetron System

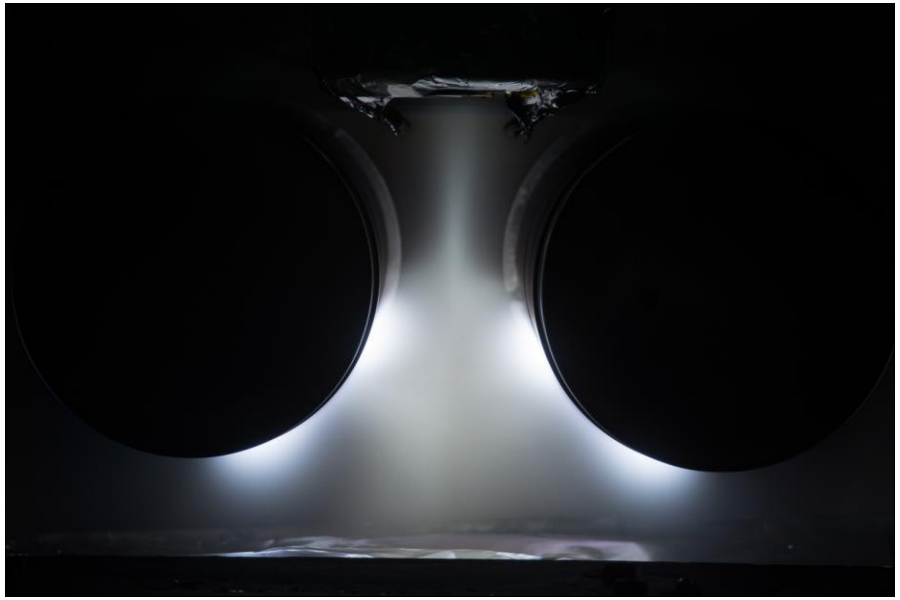


1) How we monitor H content

- **Optix remote plasma sensor**

2) How we maximise ion energy W/O bias

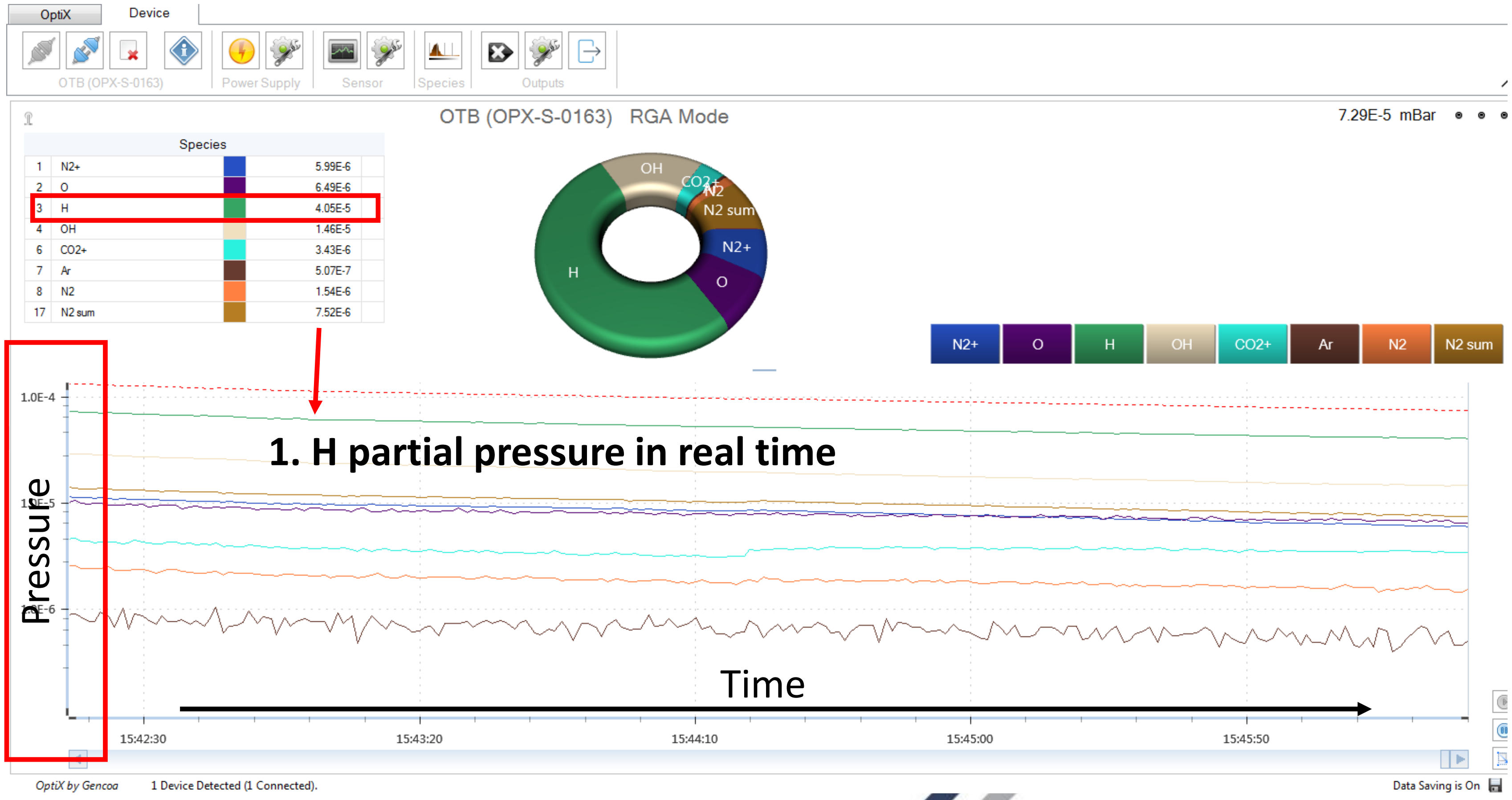
- **Gencoa Active Anode**



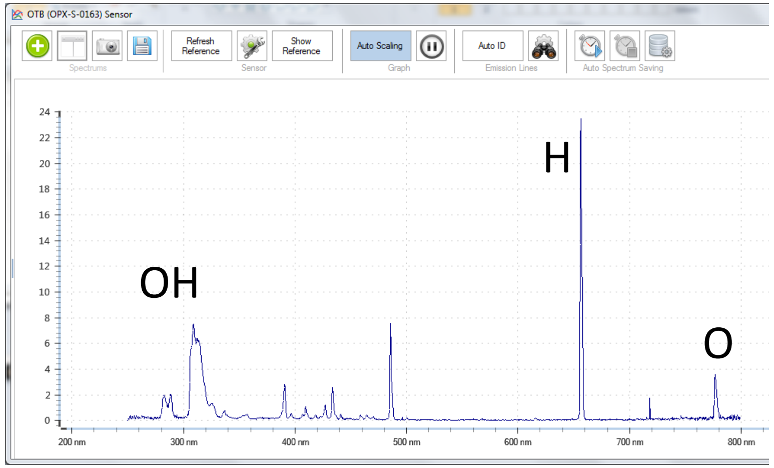
- Dual rotatable graphite electrode 475 mm
- AE Ascent Square Wave supply

II - DLC Production: Optix time resolved H tracking

- Gencoa's remote plasma sensor, ***Optix***, allows time resolved partial pressure measurements to be made



2. Live spectrum of species during pumpdown



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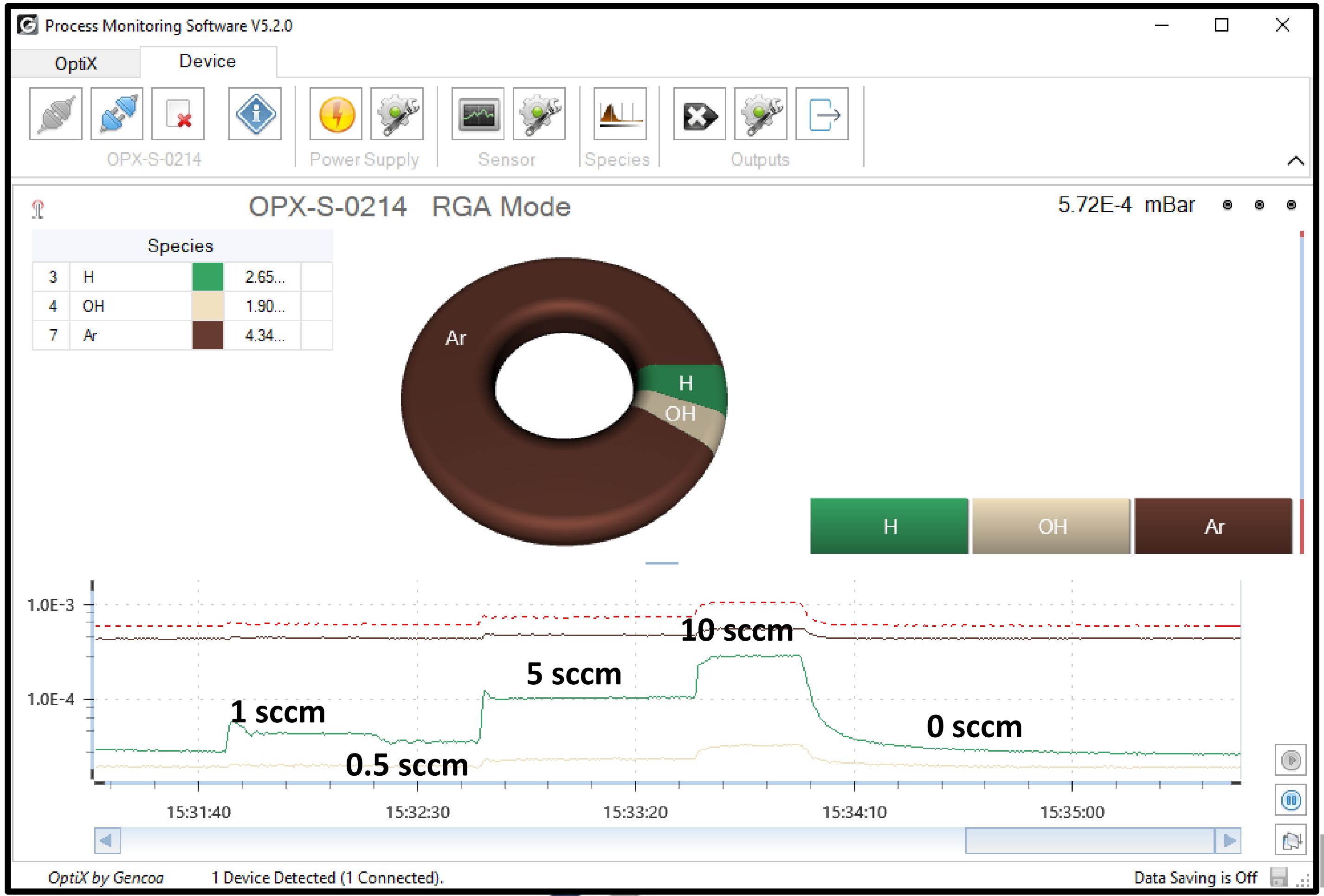
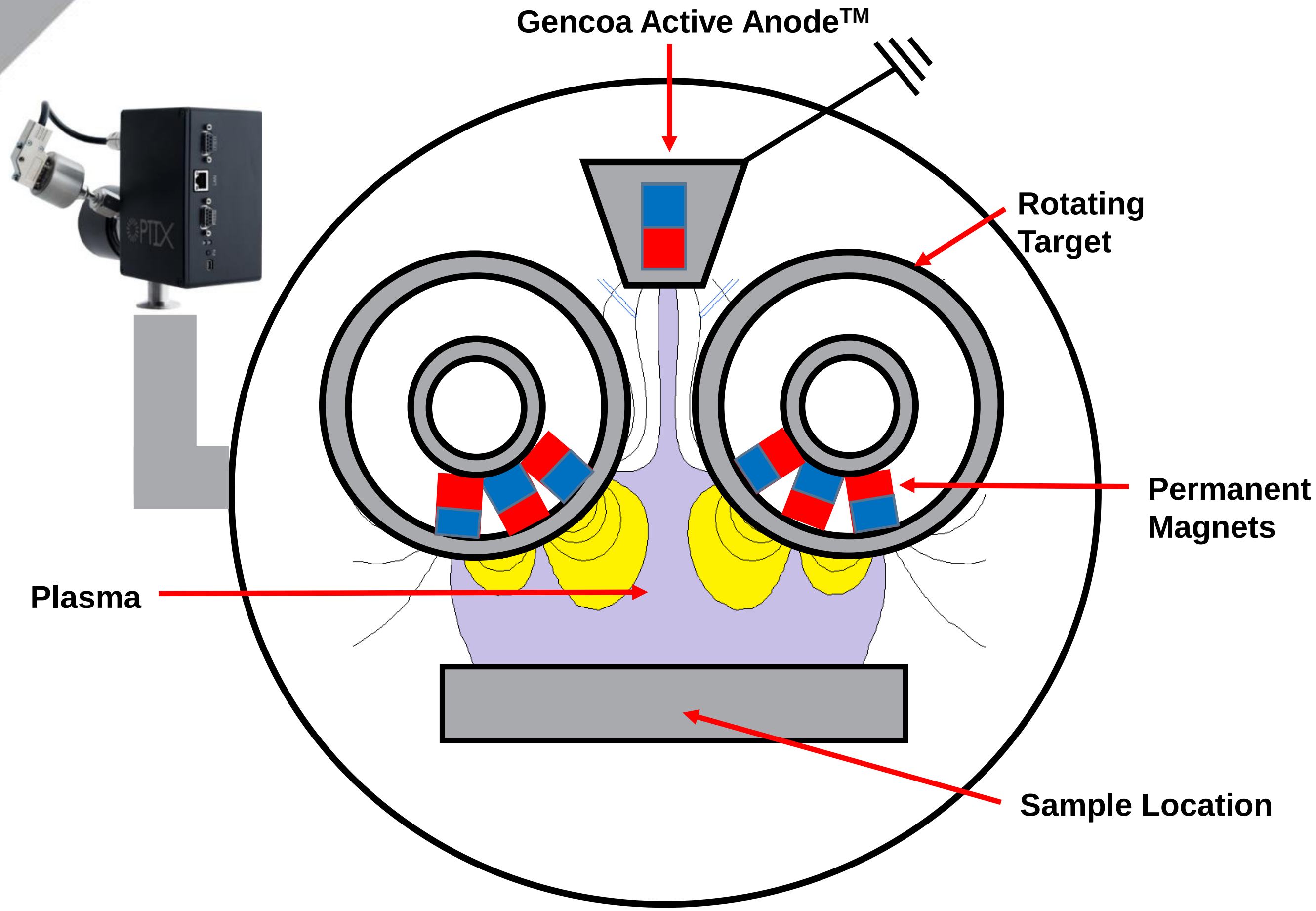


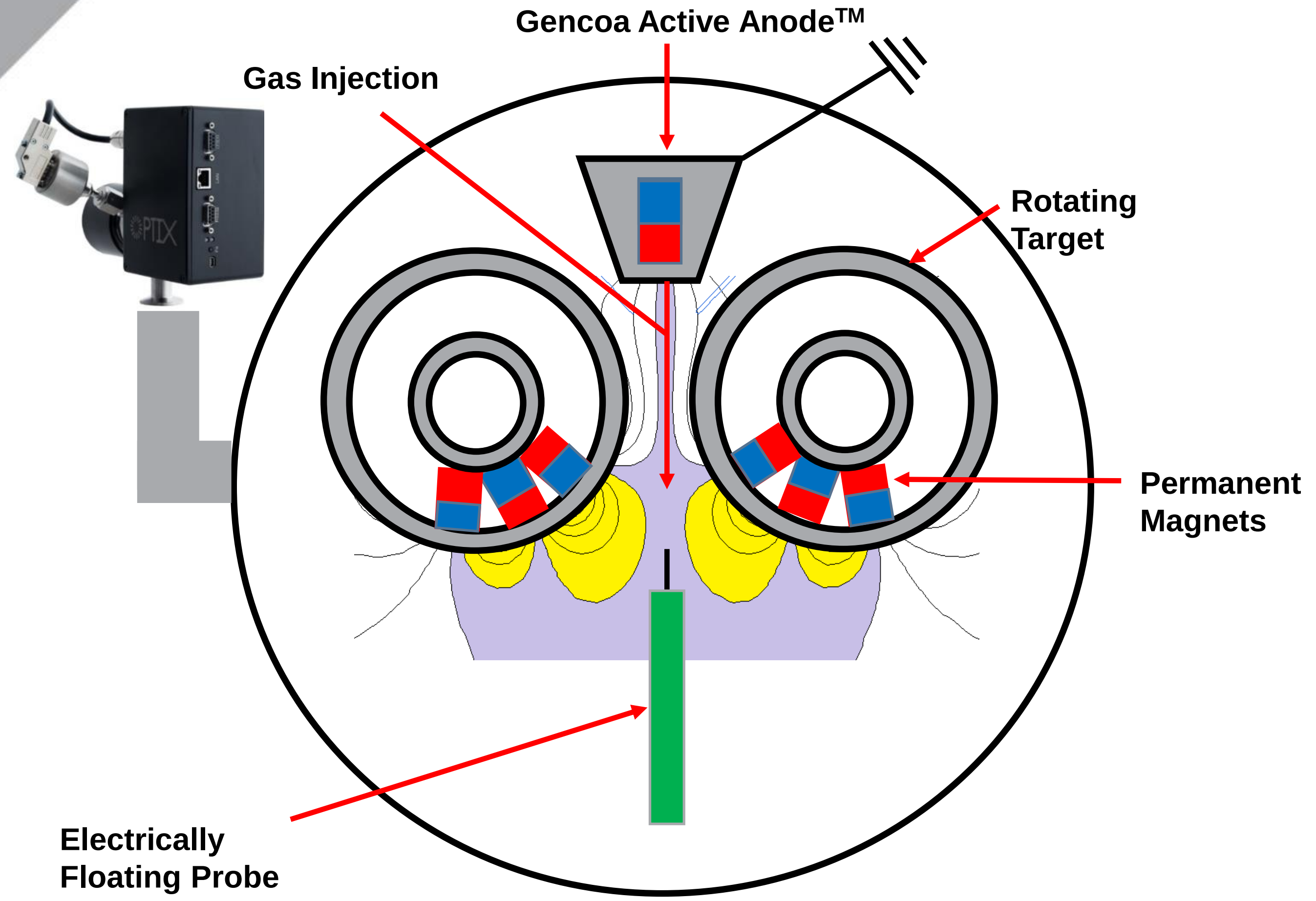
3. Varying (0-10 sccm H) flow into vacuum system

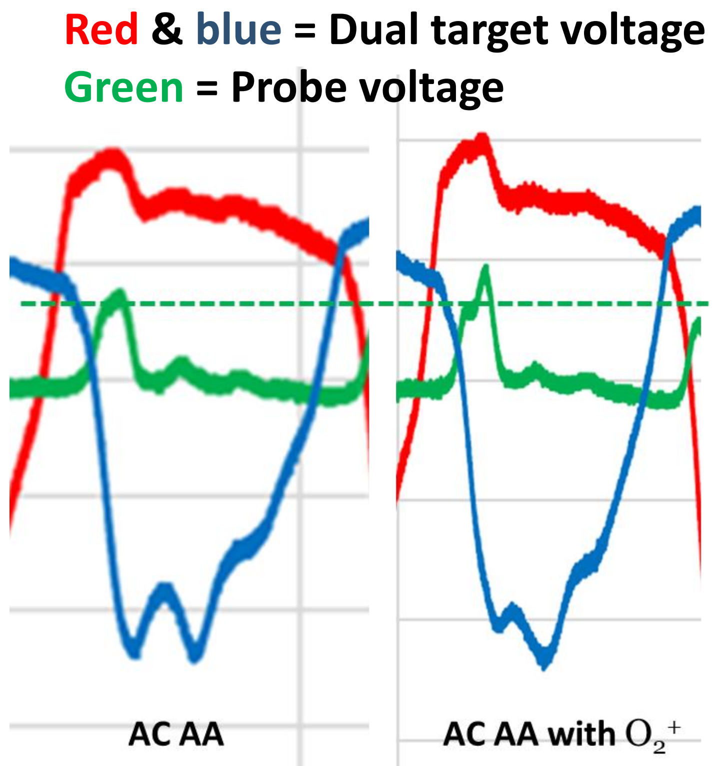
II - DLC Production: Ion Energy Enhancing (Active Anode)



- ❑ **Magnetic trap** confines plasma in narrow column
- ❑ Attracts electrons, controls temperature at substrate – **less graphitic**
- ❑ Ion bombardment enhanced through **gas injection** and **magnetics**

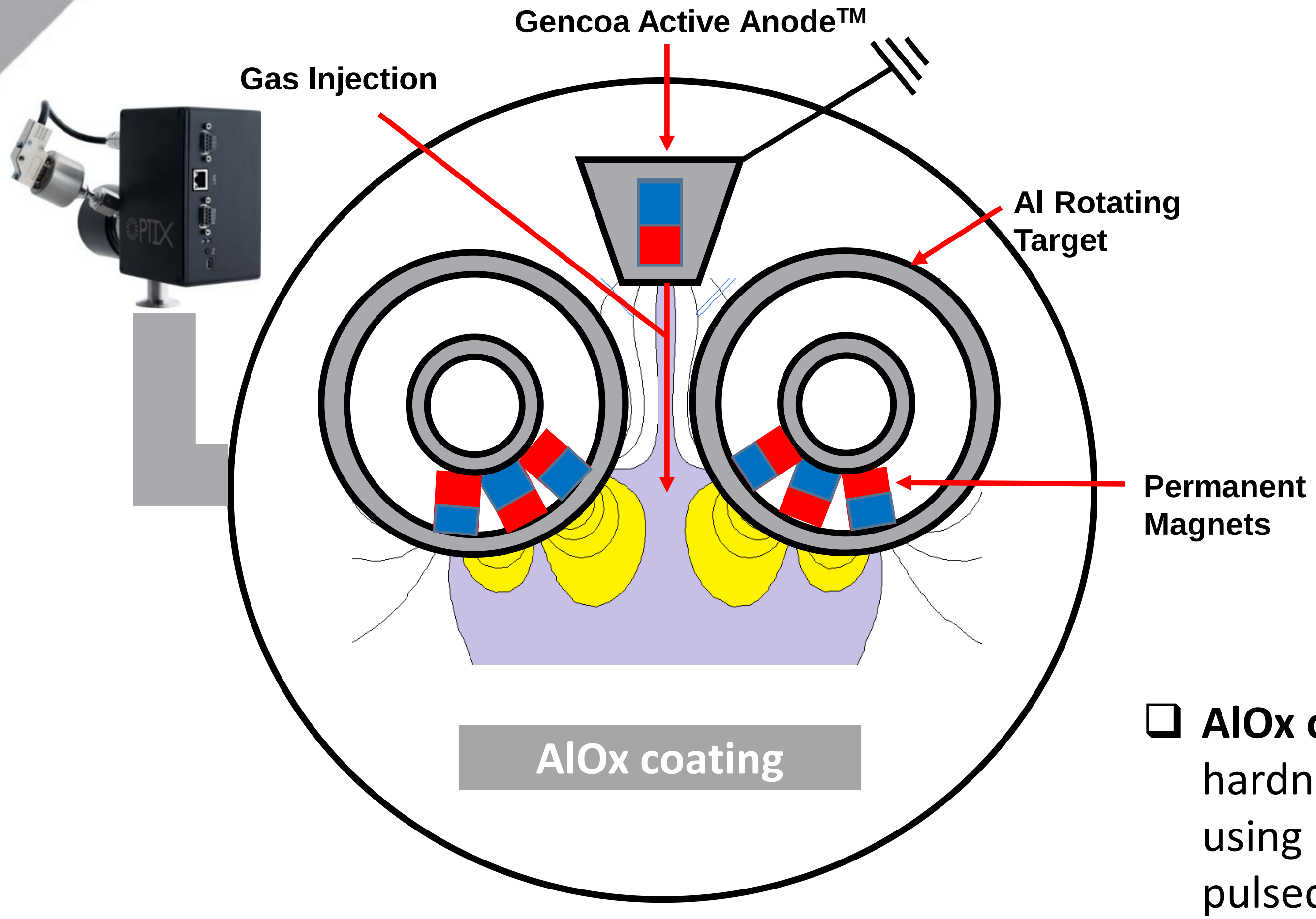
II - DLC Production: Ion Energy Enhancing (Active Anode)

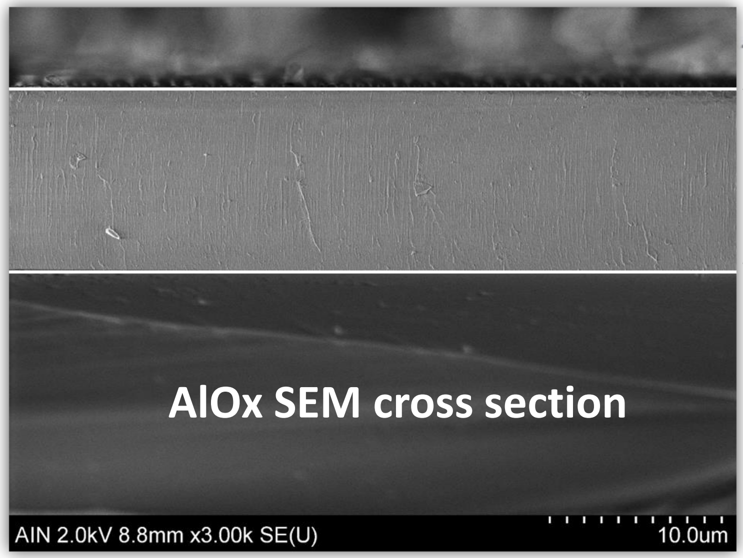




- ❑ Floating voltage probe shows **increased ion current to substrate with active anode and gas injection**

II - DLC Production: Ion Energy Enhancing (Active Anode)



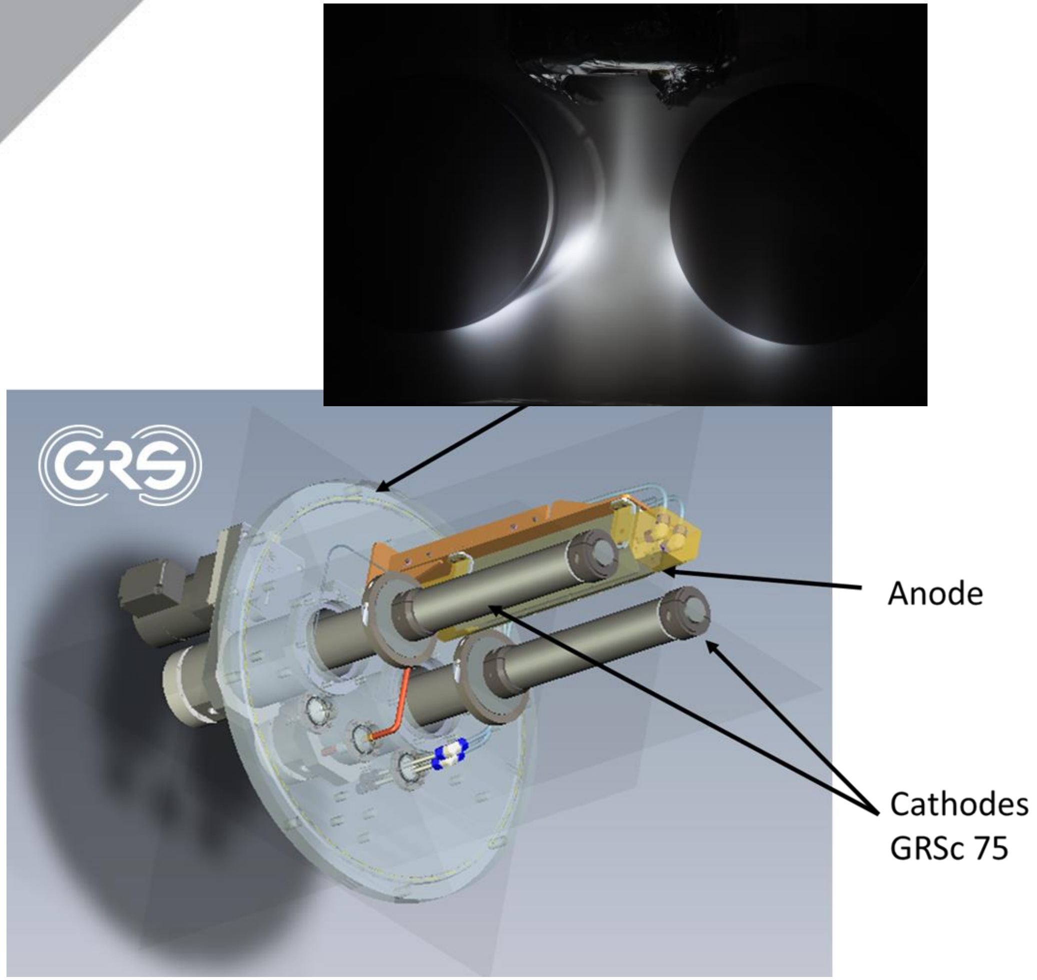


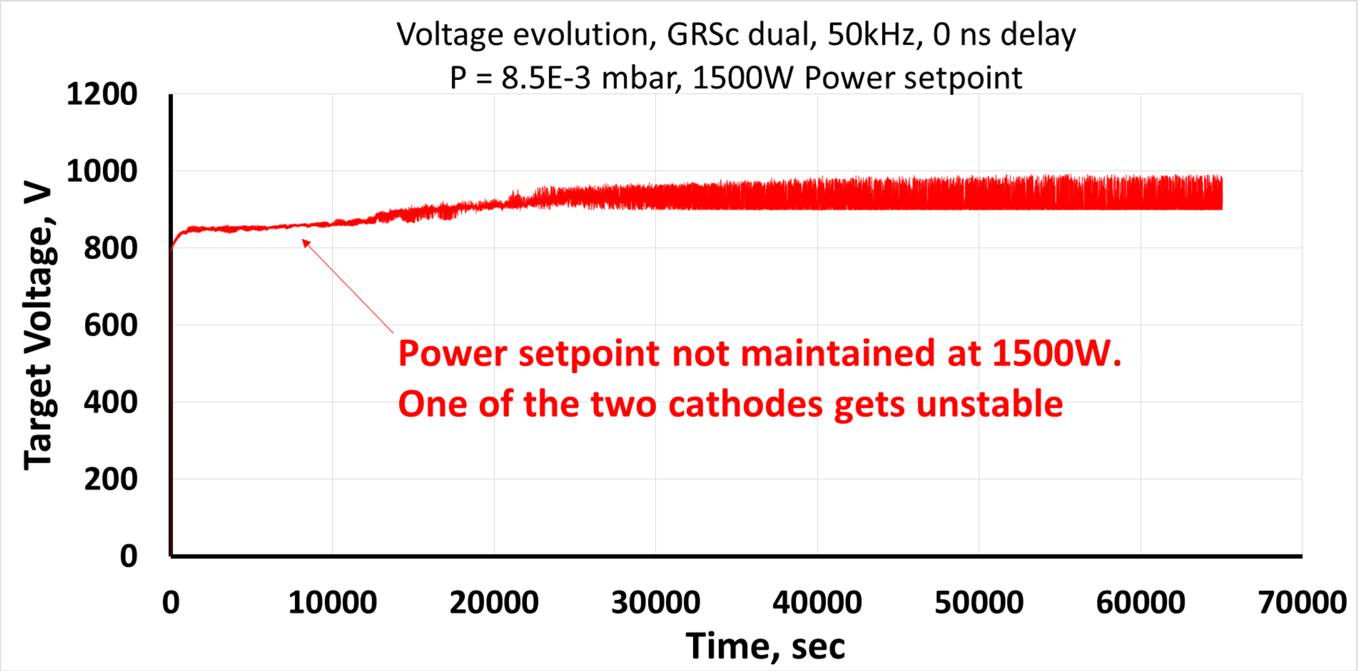
✓ **High Density Coating with AA**

- **AlOx coatings** show **superior** hardness when produced using **active anode** in DC pulsed and AC system

SAMPLE	HARDNESS (GPa)
DC-Pulsed no-anode	10.7
DC-Pulsed Biased anode	12.1
AC no active anode	11.6
AC active anode	13.1

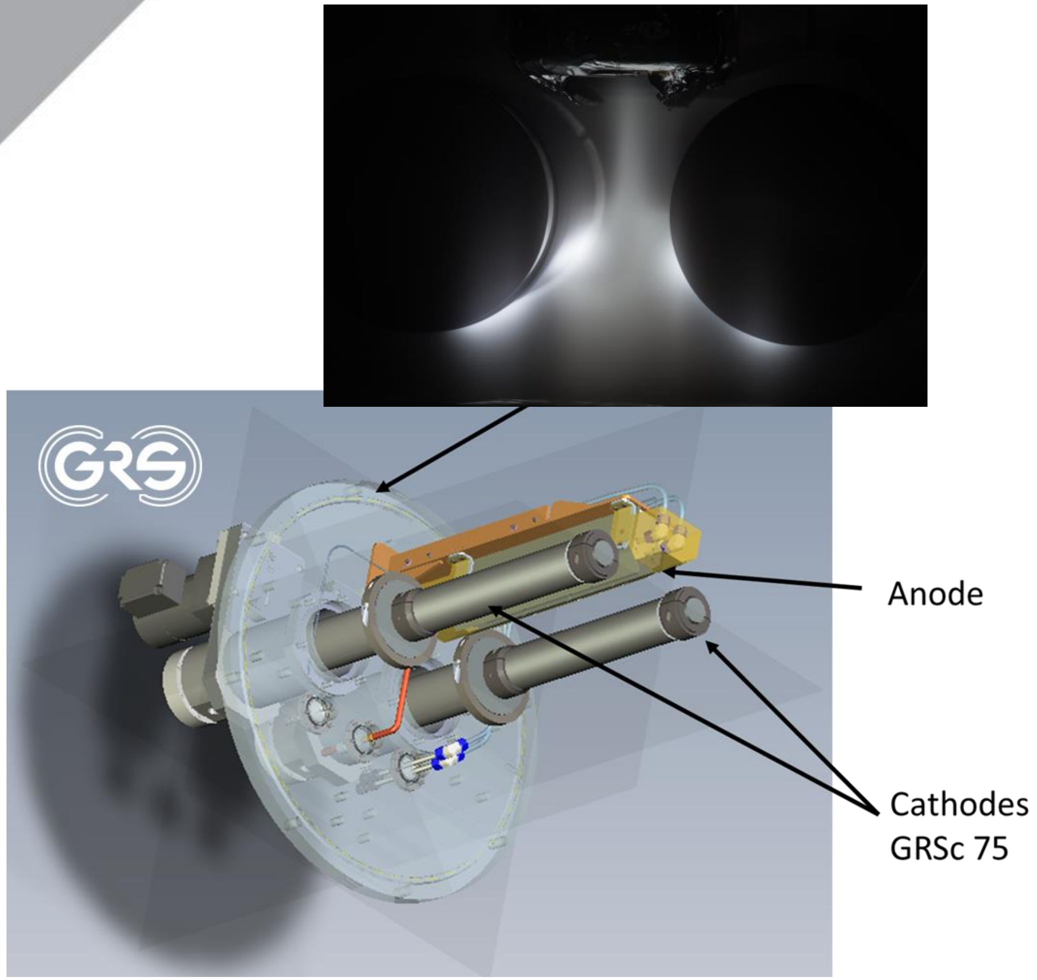
II - DLC Production: Stability with O2 Cycling

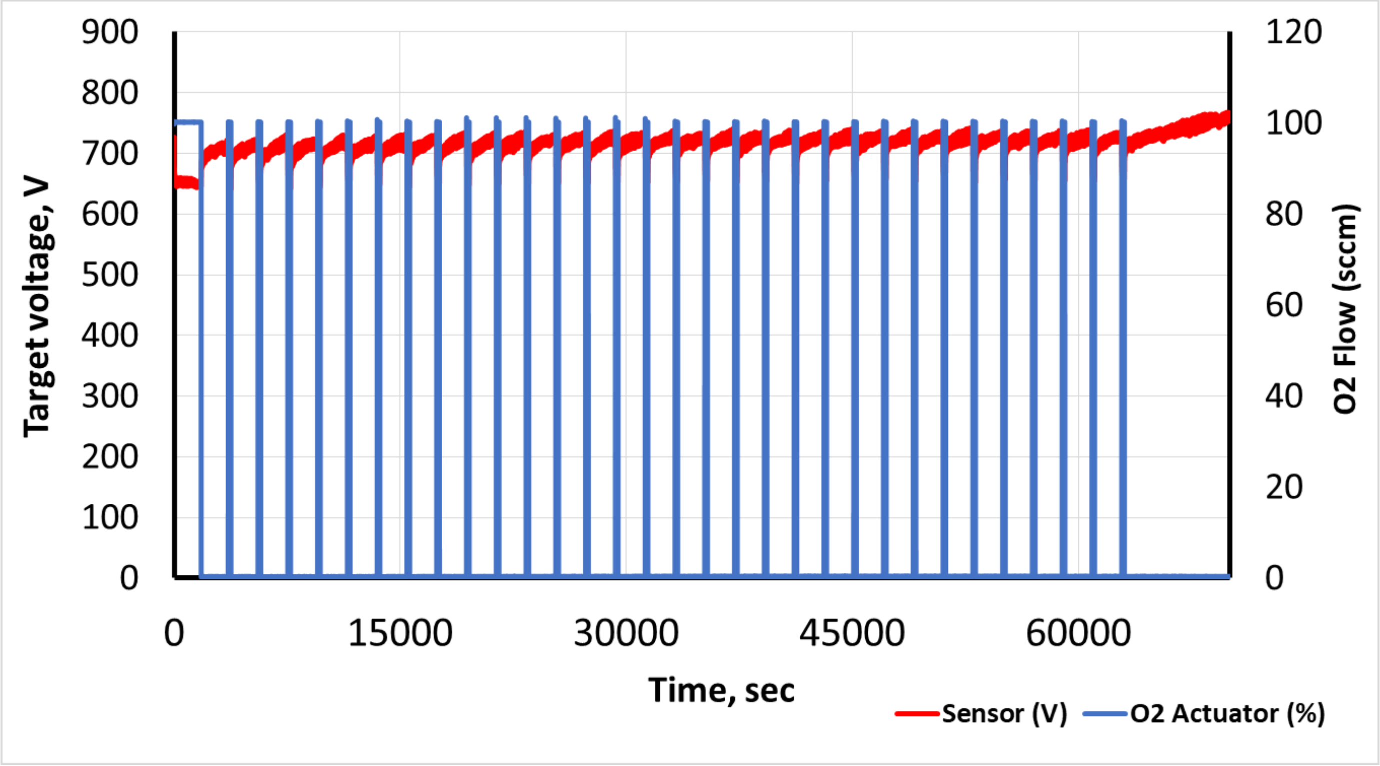




- ❑ **Voltage increases** on targets can make **production unreliable**

II - DLC Production: Stability with O2 Cycling

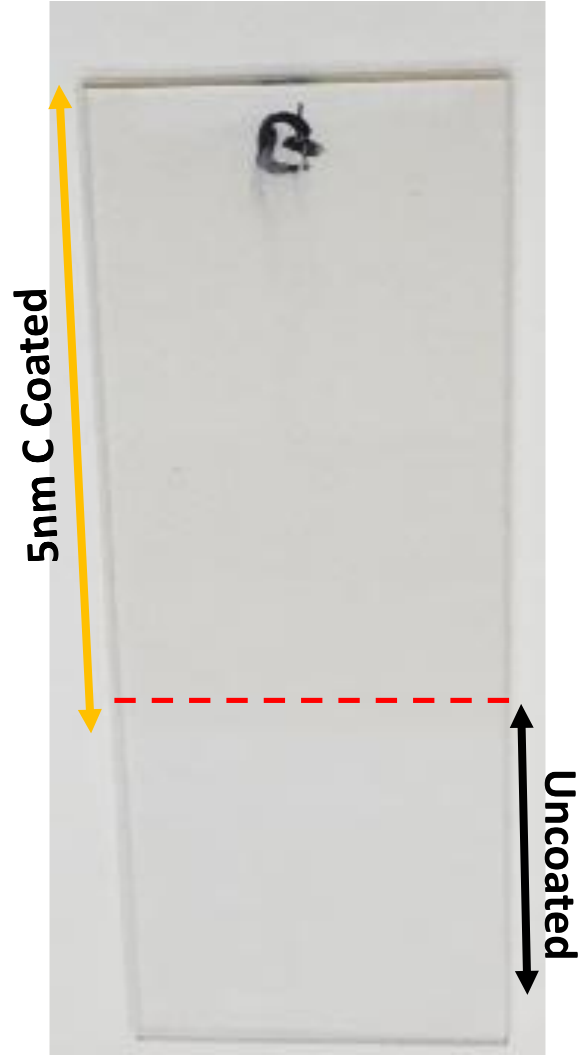




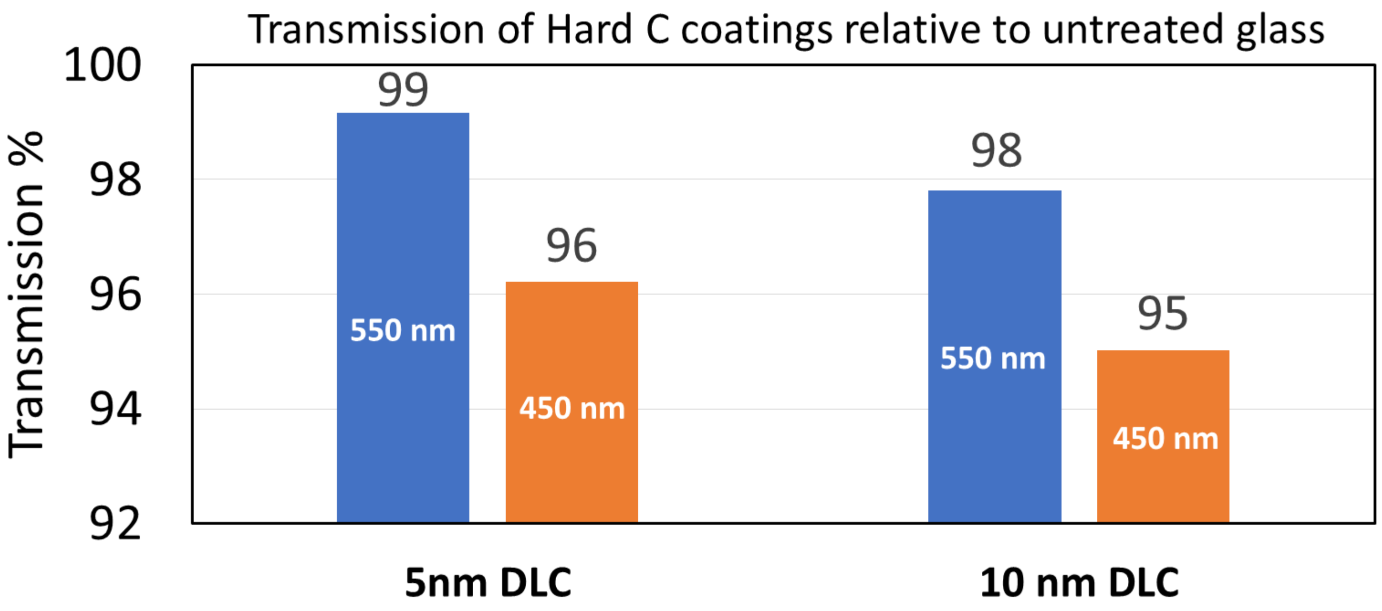
✓ Periodic O2 cycling eliminates target voltage variation

III - DLC Properties: Optical

1. Glass appearance



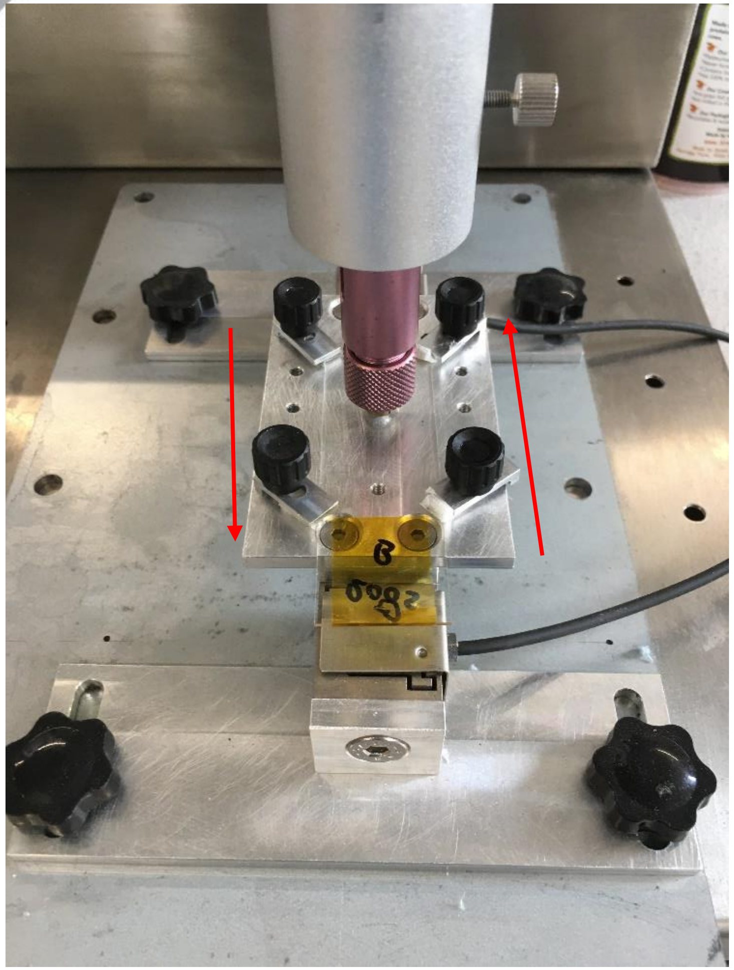
2. Transmission in visible wavelengths



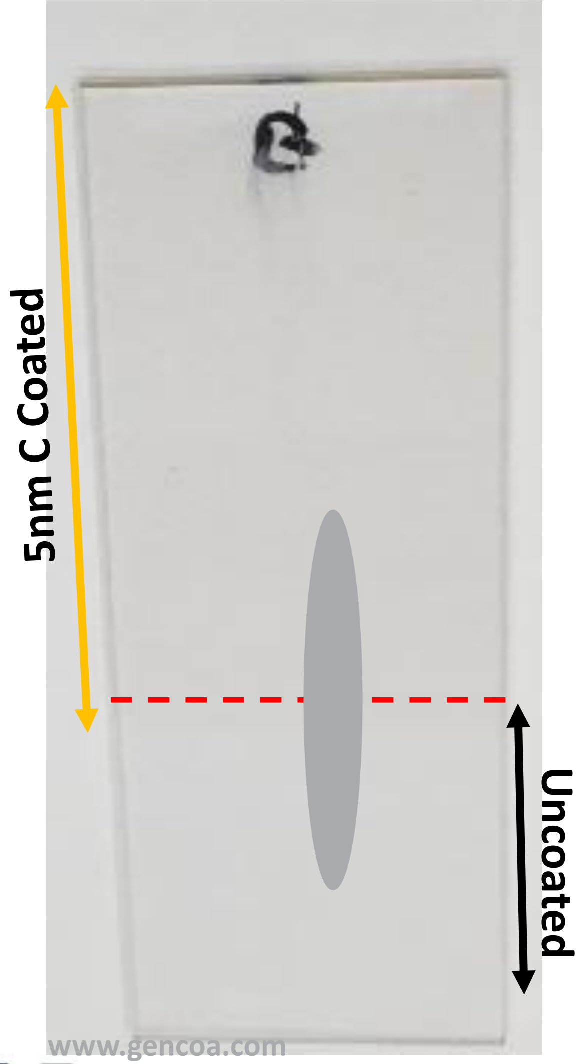
- **1-2% transmission loss** at 550 nm
- **4-5% transmission loss** at 450 nm

III - DLC Properties : Reciprocating Abrasion

1. Reciprocating Abrasion Test

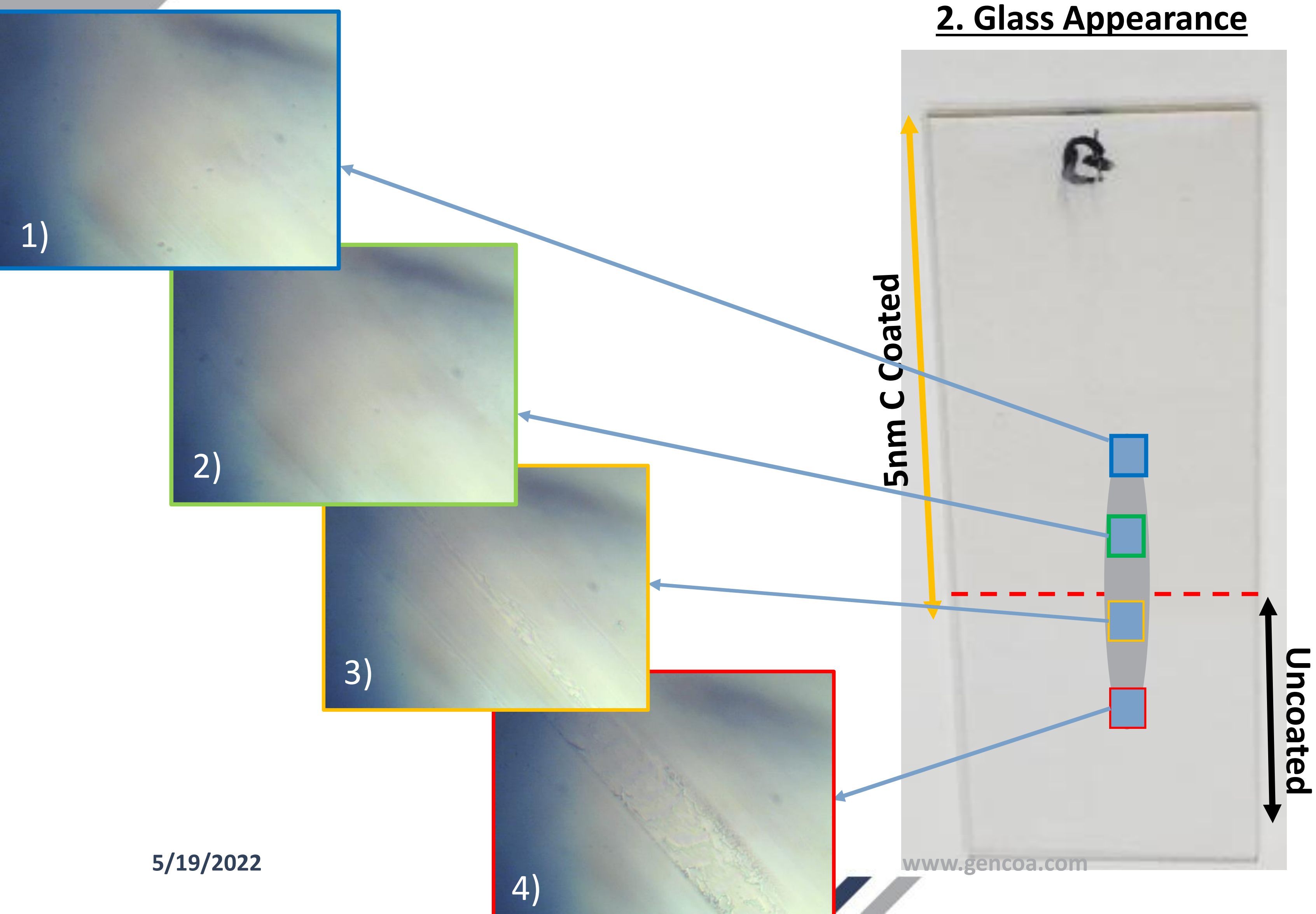


2. Glass Appearance



Abrasion Test Parameter
0.5kg, WC/Co ball 6 mm,
20 per min, 200 passes

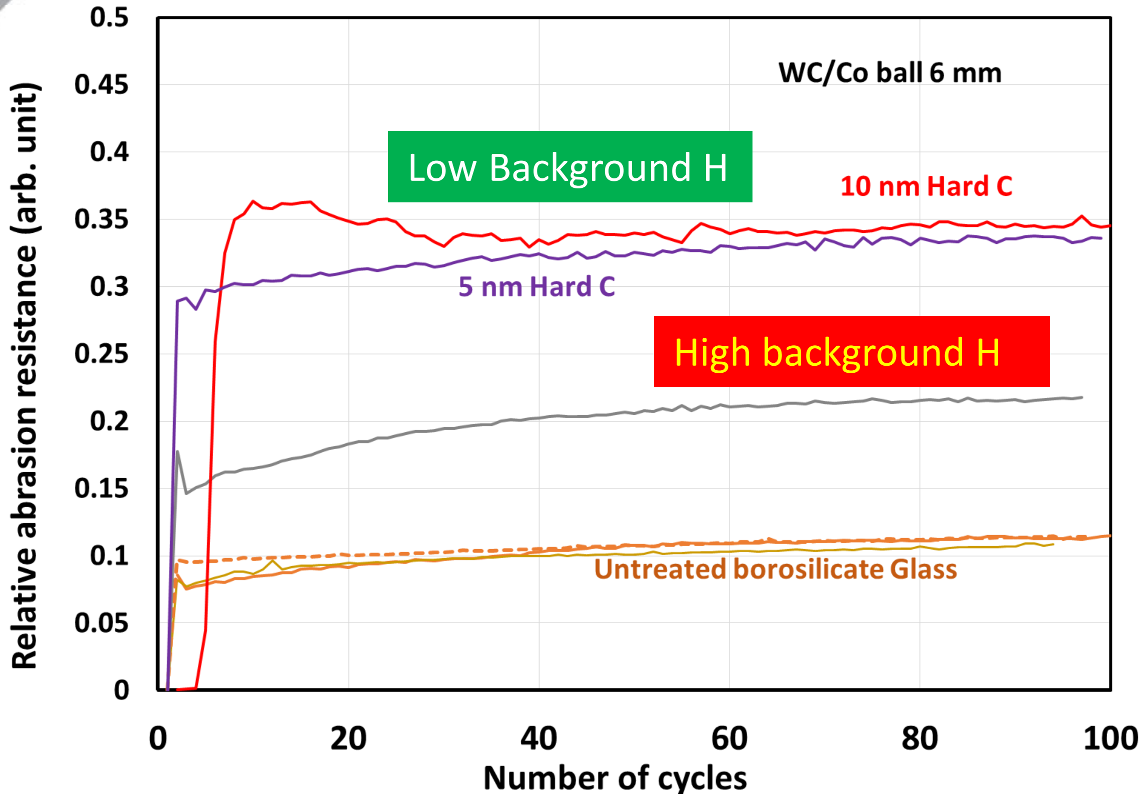
III - DLC Properties : Reciprocating Abrasion



1. Reciprocating Abrasion Test Result

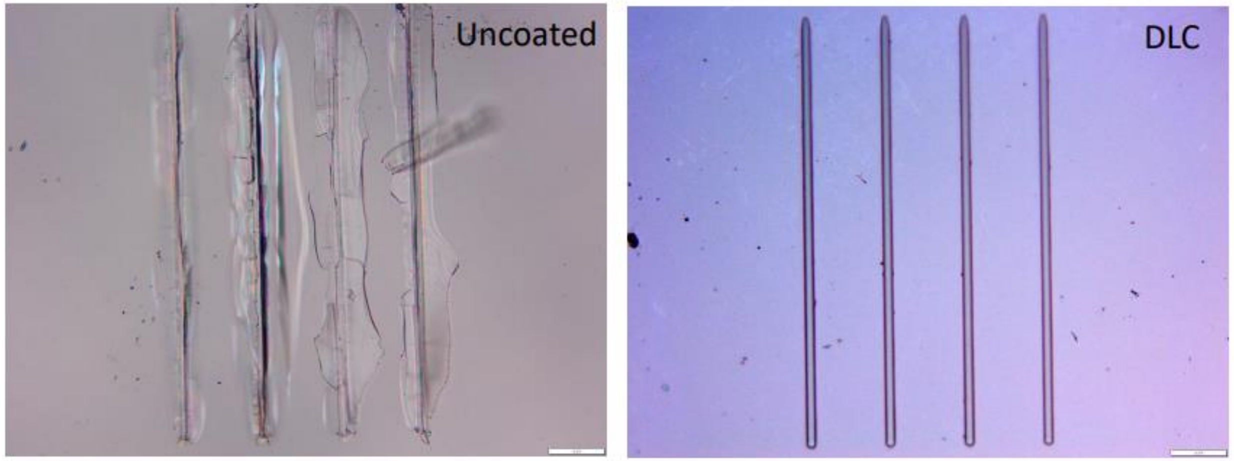
- Clear **fracture under 0.5kg abrasion test on uncoated glass**
- **Less pronounced, smooth depth** profile of scratch on DLC
- **Low friction of DLC**
- **Abrasion resistance of DLC**

III - DLC Properties : Abrasion Resistance and Scratch Test



Constant load scratch test

- Diamond conical tip
- 300 mN
- 10nm DLC



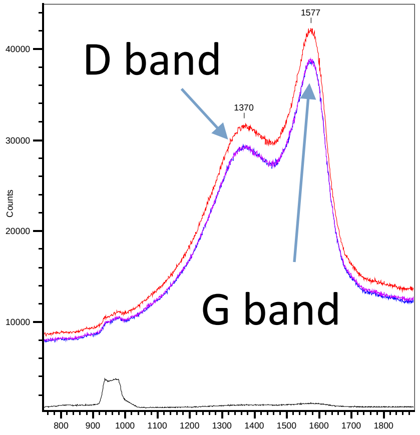
- ❑ **Critical scratch load resistance under low loads** for DLC relative to uncoated boro. glass

- ❑ **3x abrasion resistance of 5-10 nm DLC** relative to uncoated glass
- ❑ Lower H content produces more abrasion resistant DLC

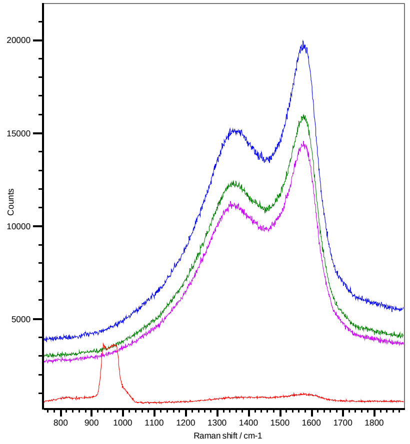
III - DLC Properties: O2 feedback control

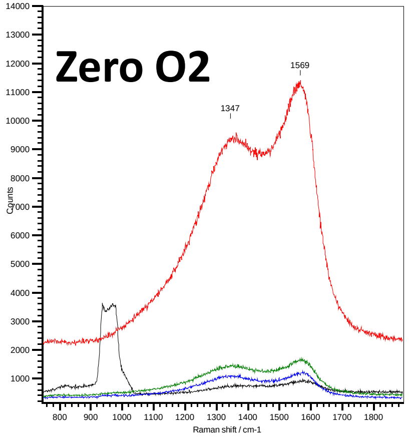
- **Raman Spectroscopy**

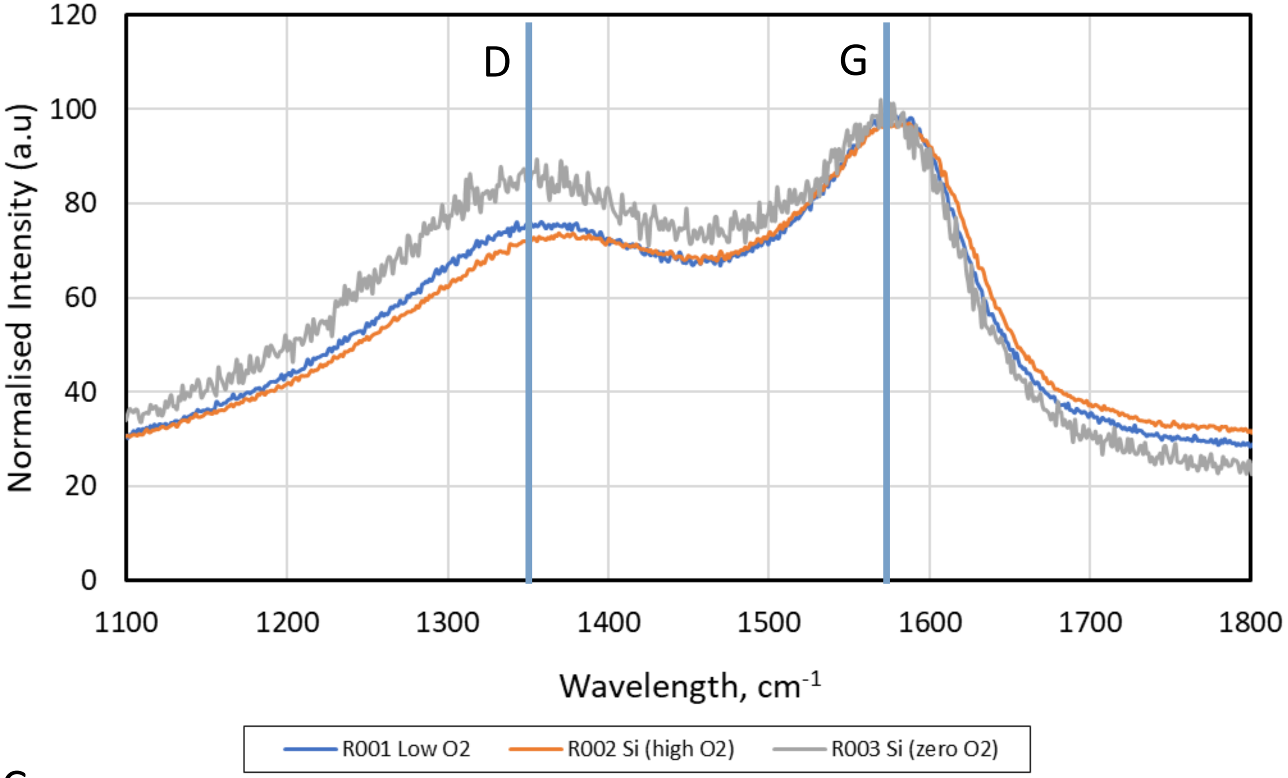
High O2 excess



Low O2 excess





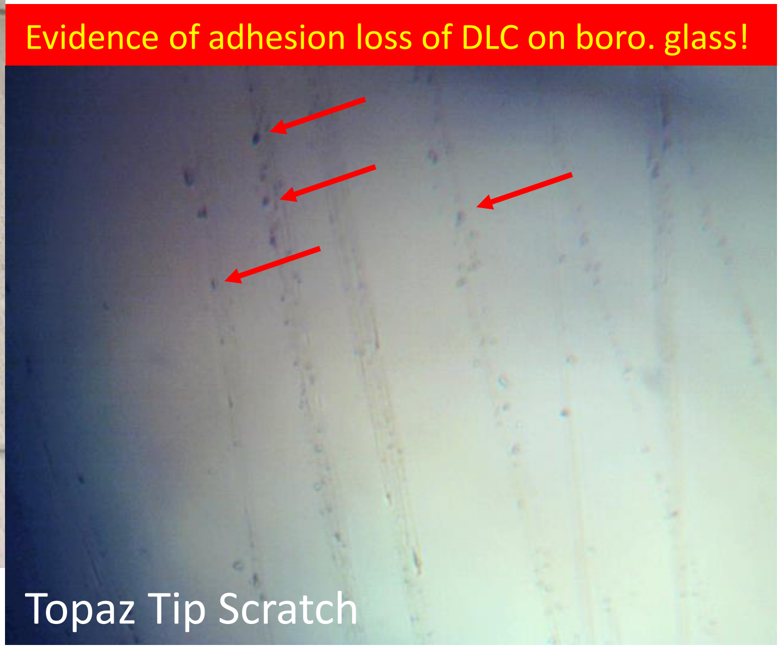


- ❑ O2 excess flow during DLC production **better for increasing sp3 bonding**

	High O2 excess	Low O2 excess	Zero O2
I(D)/I(G)	0.72	0.75	0.86

IV- Drawbacks to DLC : Adhesion

One of the main drawbacks of DLC coatings is their high intrinsic compressive stress. It can reach tens of GPa which alters their adhesion and limits the thickness of coatings, resulting in the **peeling off** of the coating.

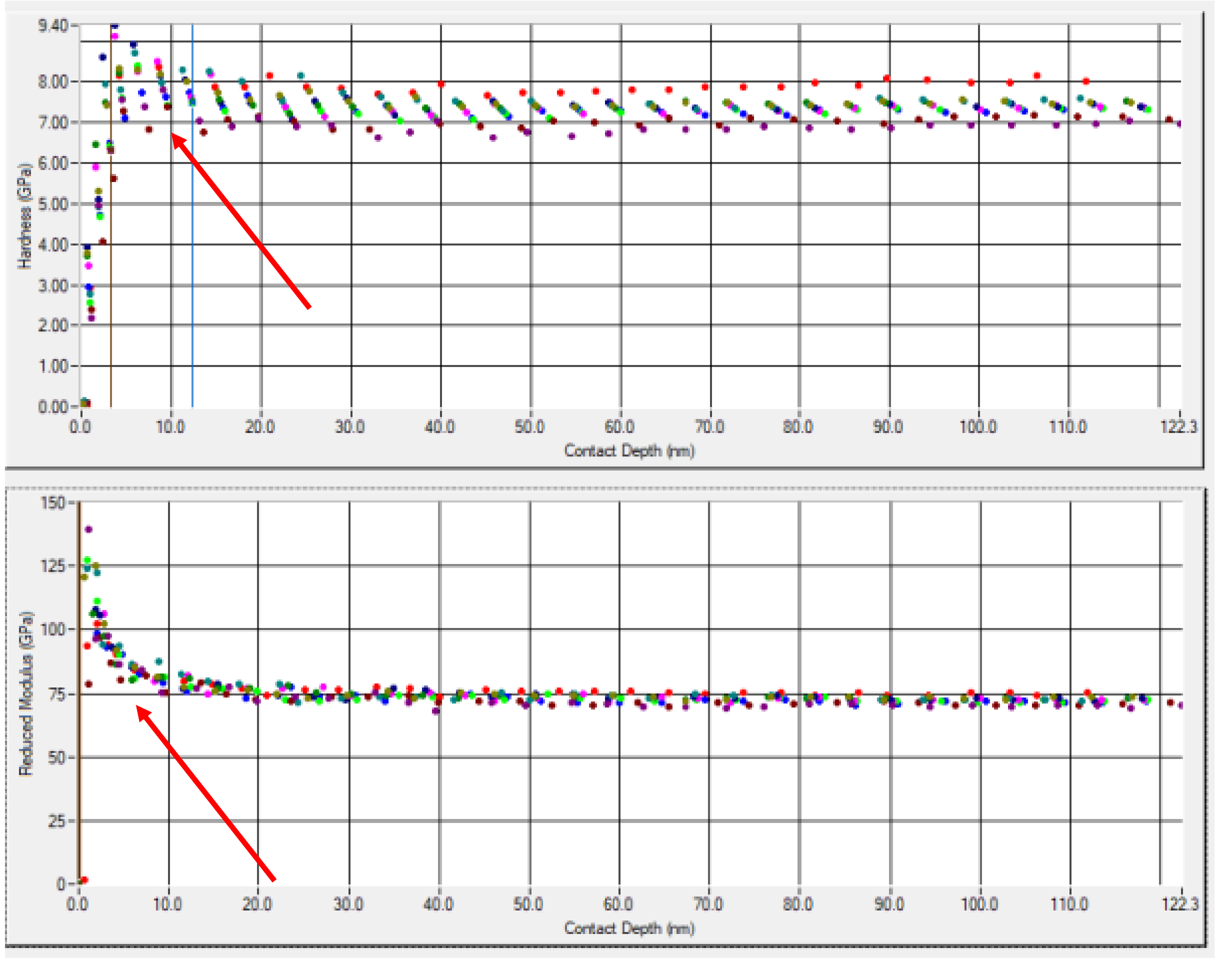


Solutions

- ➢ **Doping DLC with metals**, Ni or Si (loss of transmission)
- ➢ **Bias-graded deposition** (Glass can't bias!)
- ✓ **Deposit an intermediate layer between the substrate and the DLC film** in order to increase the adherence and reduce the intrinsic stress in the interface DLC/substrate.

IV- Drawbacks to DLC : Hardness with Depth

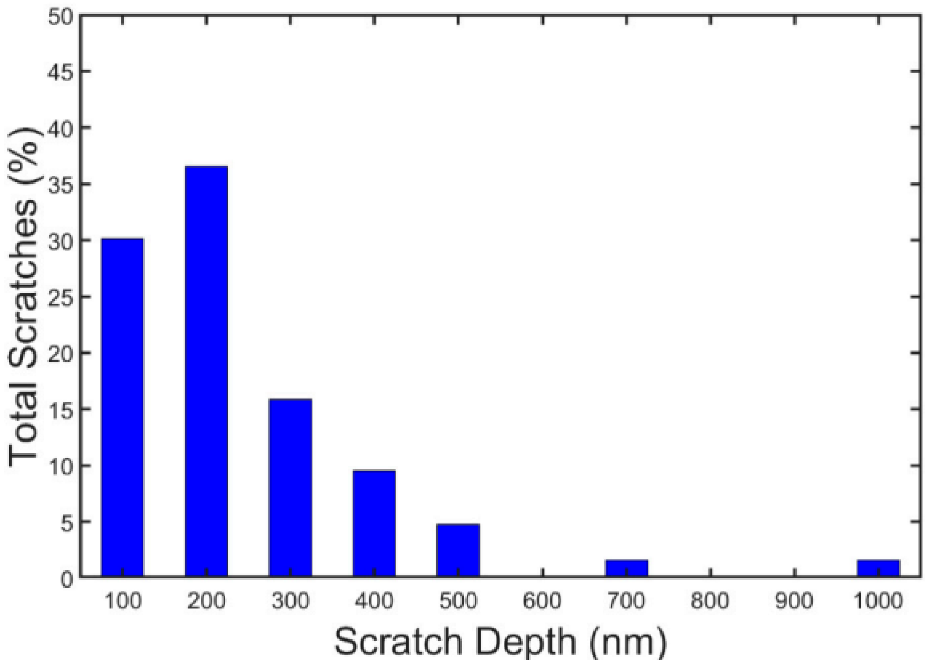
Hardness vs depth test

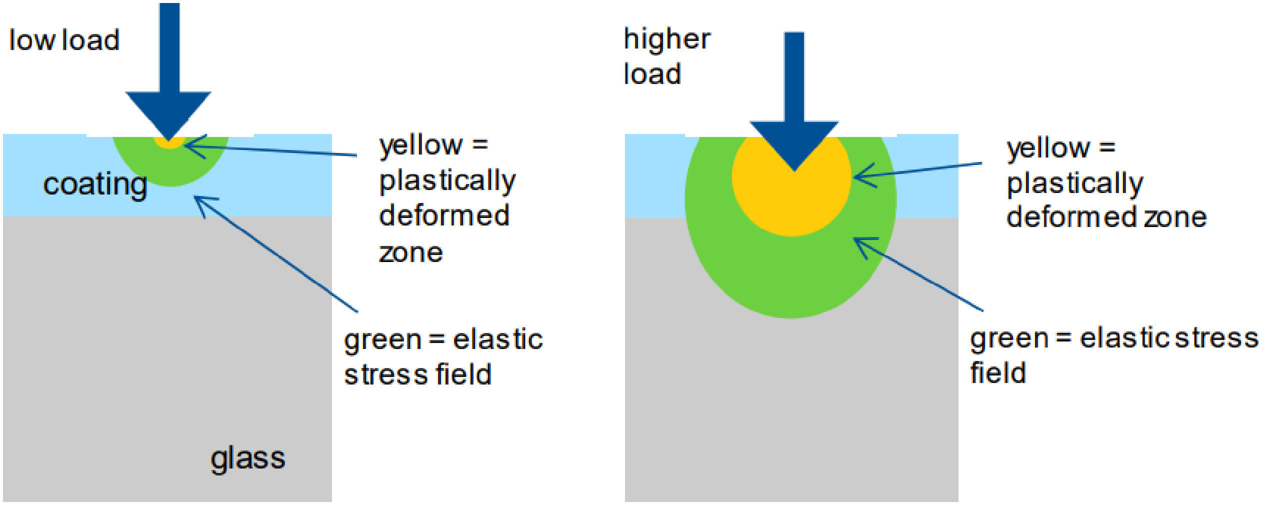


Coated DLC

- ❑ **Hardness is only maintained in first nm of coating**
- ❑ Hardness is key to preventing deformation
- ❑ <u>**Need intermediate layer**</u> between DLC and glass

IV- DLC + Interlayer: Maintaining Hardness



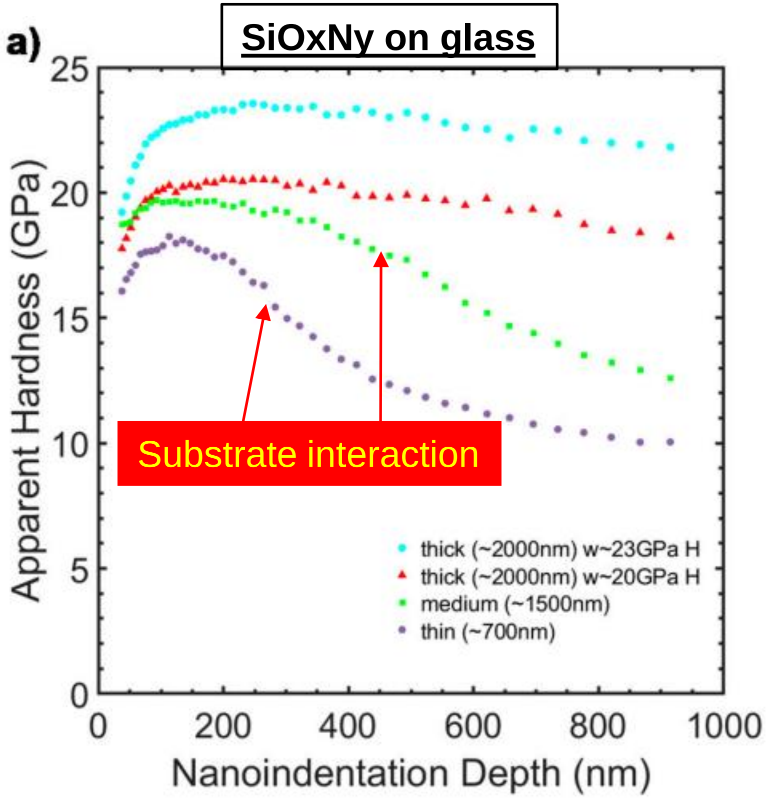


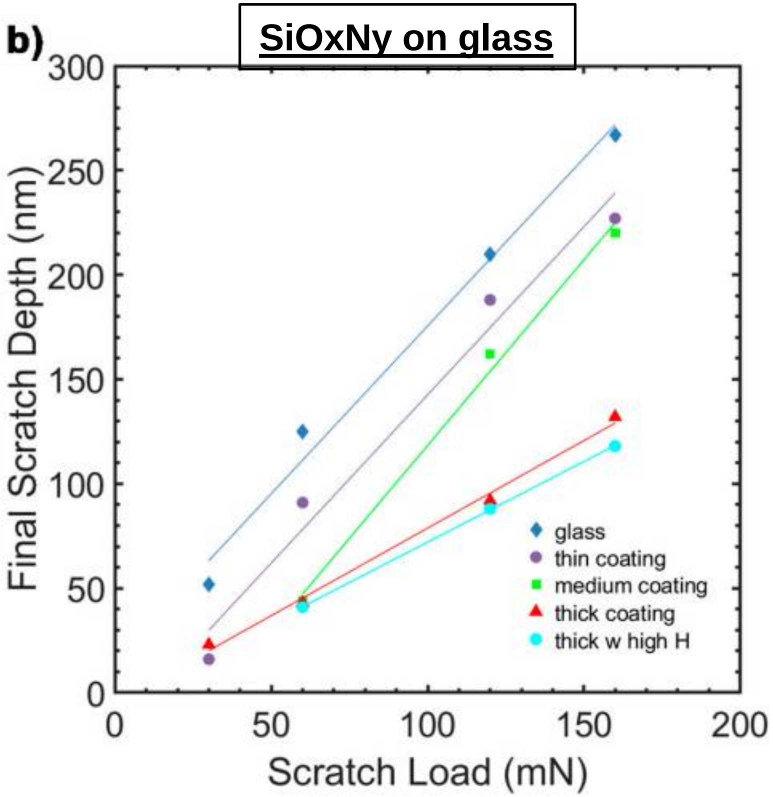
(1) Price, J.J et al, Nanoindentation Hardness and Practical Scratch Resistance in Mechanically Tunable Anti-Reflection Coatings. *Coatings* **2021**, *11*, 213

- ❑ Data taken from (1) - Measured **scratch depths** of micro-ductile scratches from field study of consumer electronics devices with chemically strengthened **glass covers**
- ❑ **Majority** of observed scratch depths are in **100-500 nm depth range**

IV- DLC + Interlayer: Maintaining Hardness

- ❑ **Thinner** interlayers haver **lower peak hardness** and **suppress** hardness at deeper depths
- ❑ A **thick** transition layer allows “true” hardness of film to be achieved

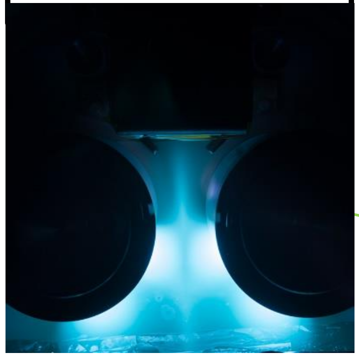




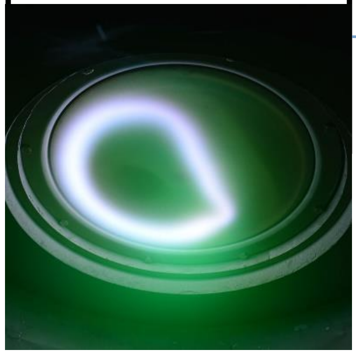
- ✓ **Reduced scratch depth** with thicker interlayer between glass and DLC
- ✓ Scratches become **invisible to human eye**

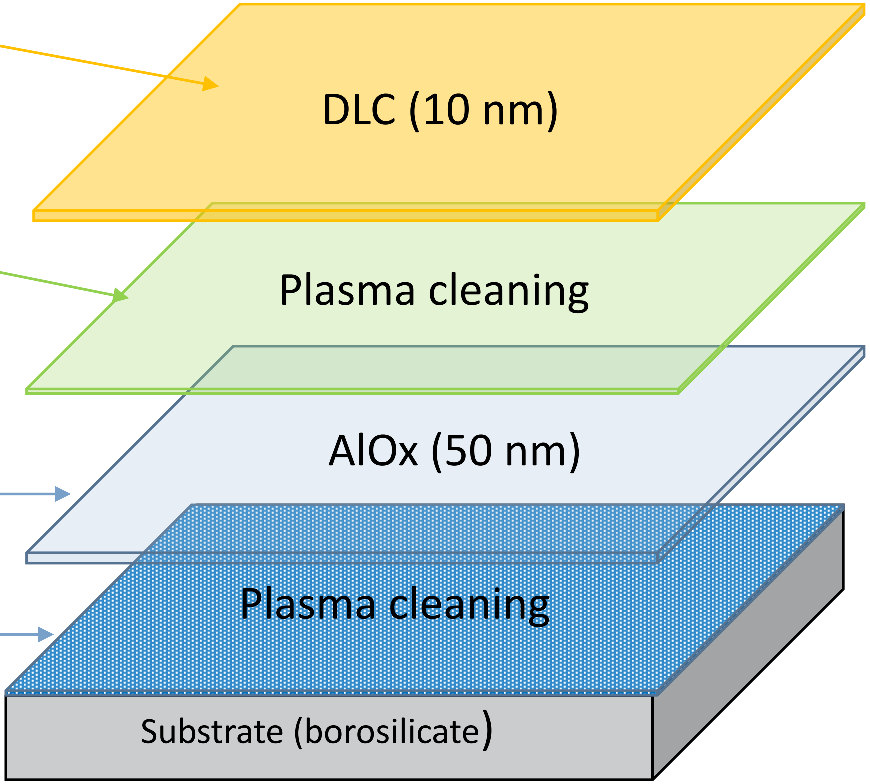
IV- DLC + Thinner Interlayer: Sapphire Scratch

2) DLC + plasma cleaning, C Dual GRSC



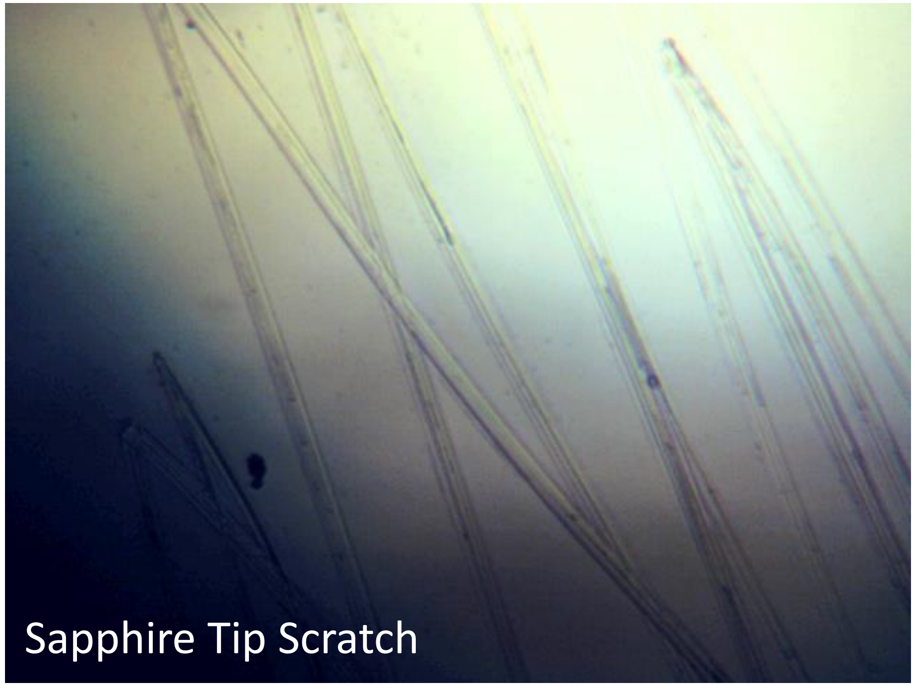
1) AlOx coatings + plasma cleaning





1) MS - FFE 75 DC Pulsed

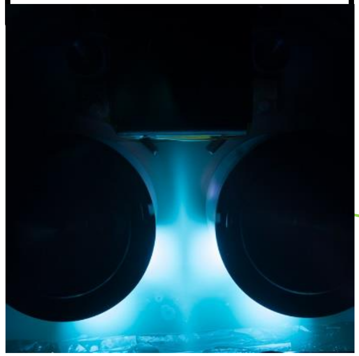
50 nm AlOx + 10 nm DLC



- Clear visible scratch under high load

IV- DLC + Thicker Interlayer: Sapphire Scratch

2) DLC + plasma cleaning, C Dual GRSC



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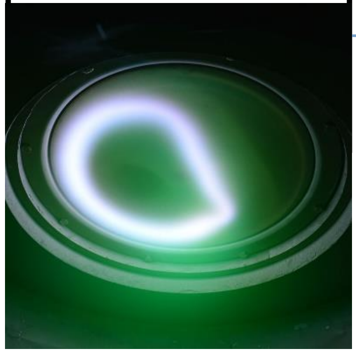
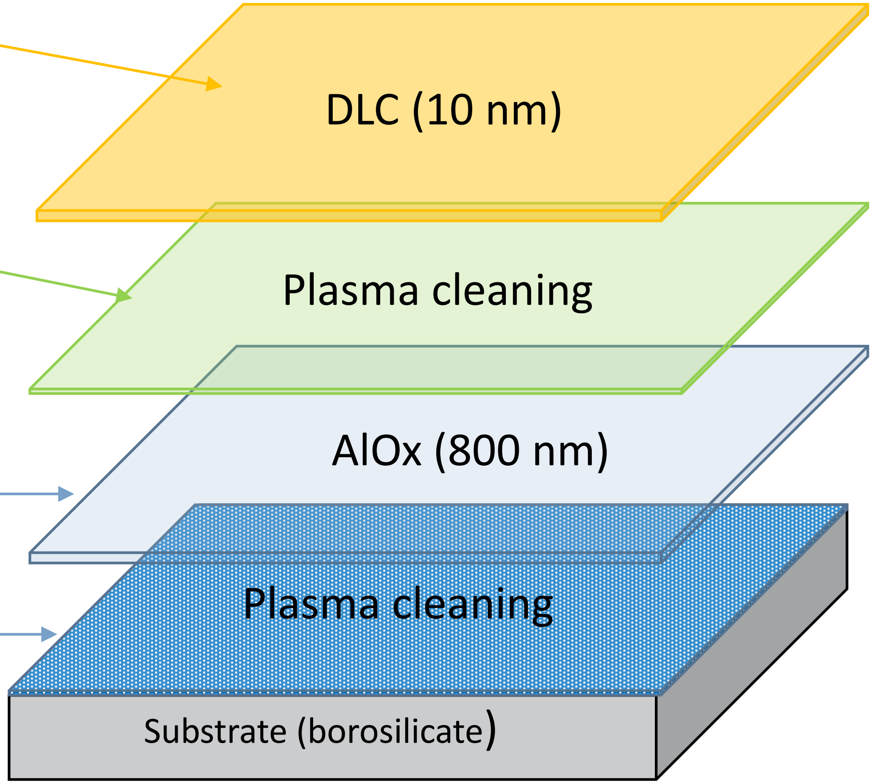


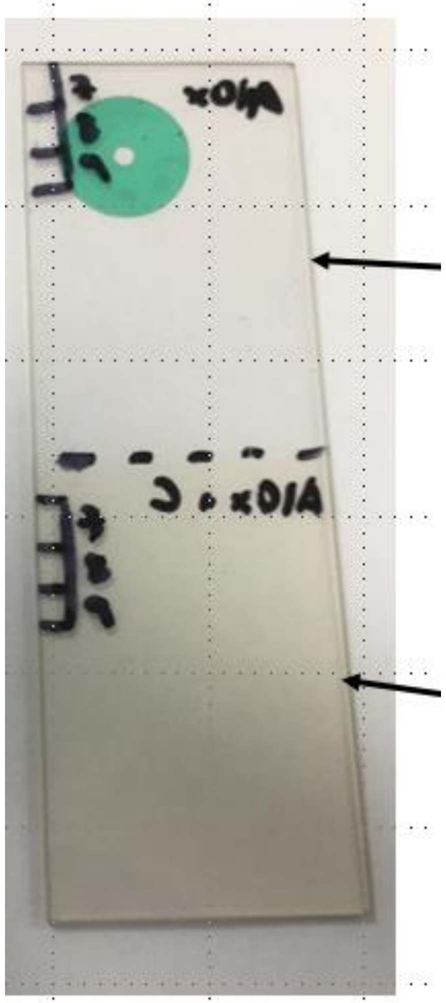


1) MS - FFE 75 DC Pulsed

800 nm AlOx + 10 nm DLC

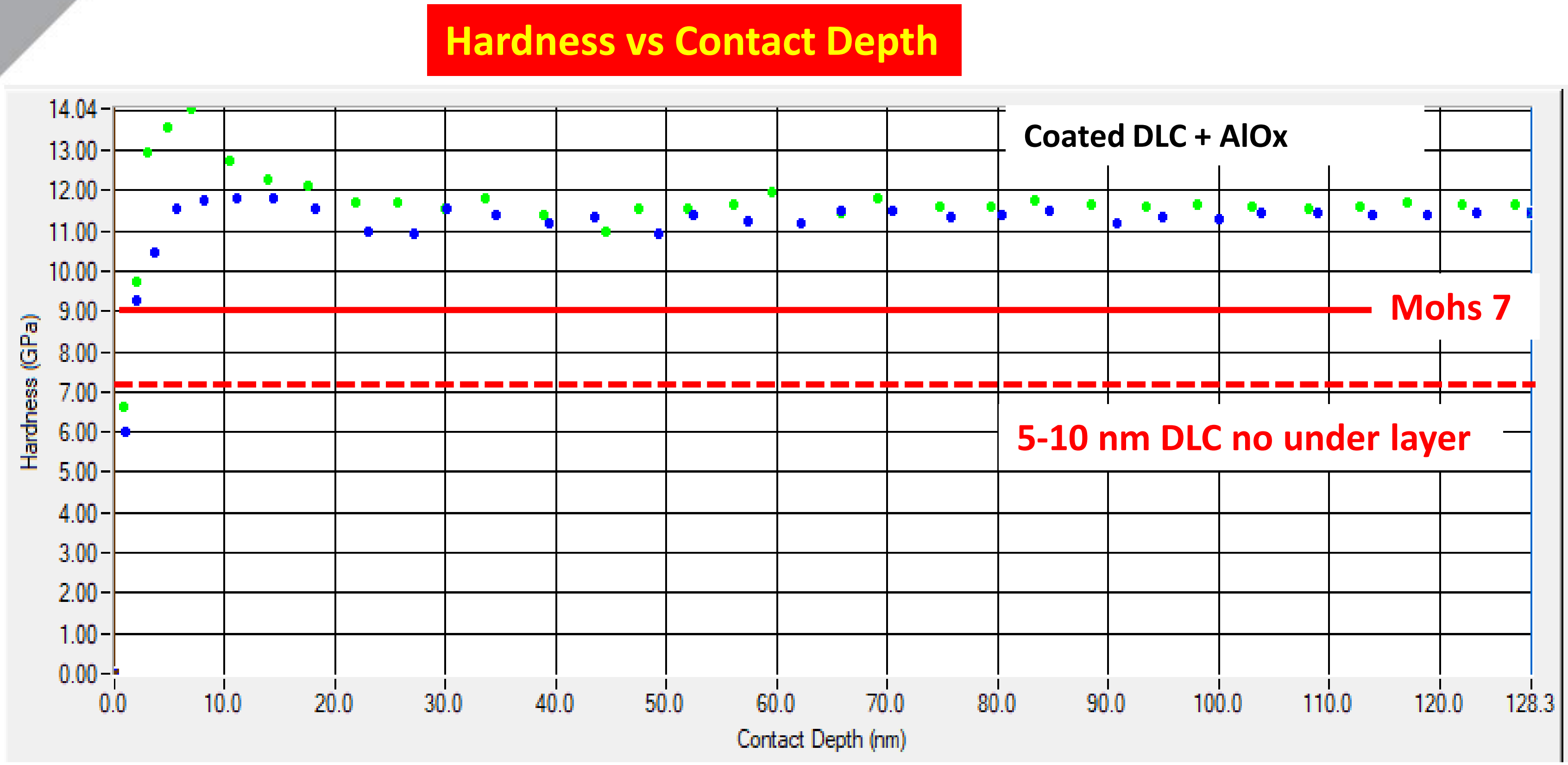
- ✓ **Scratch near invisible to human eye and O.M**
- ➢ Adhesion + coverage with thin DLC coating

IV- DLC + Thicker Interlayer: Transmission



- Transmission r.t.g – **93% at 550 nm**

IV- DLC + Thinner Interlayer: Hardness



- ✓ **Hardness** of DLC with AlOx under layer **superior** relative to just thin (5-10 nm) DLC coating - approaching Mohs 8 (~15GPa)

Summary

- Time resolved H monitoring allows H content of vacuum system DLC to be observed during DLC coating – **fast, indirect measure of H in layer**
- **Active anode** gives **increased ion energy bombardment** at substrate surface without electrical substrate bias
- **3x abrasion resistance of DLC relative to borosilicate glass** produced with rotatable system, H monitoring and active anode
- O2 presence in process, important to **lower sp2/sp3** ratio and **eliminate target voltage variation**
- Transition layer vital to maintain hardness and reduce deformation **– improving scratch resistance under high loads**

Future - Optimising transition layer thickness and adhesion of AlOx-DLC needed to reach > Mohs 8

GENCOA

Thank you for your attention!

Dr. Patrick McCarthy

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