Deposition of hard highly transparent abrasion-resistant DLC on glass

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Content of presentation

- Carbon sputtering, HIPIMS discharge and effect of positive voltage reversal
- Deposition of carbon from a dual rotatable magnetron
- Importance of electron extraction, magnetic guidance
- Hard coatings on insulating substrates: DLC on glass with Hipims and Switching Power

Introduction – Carbon by magnetron sputtering

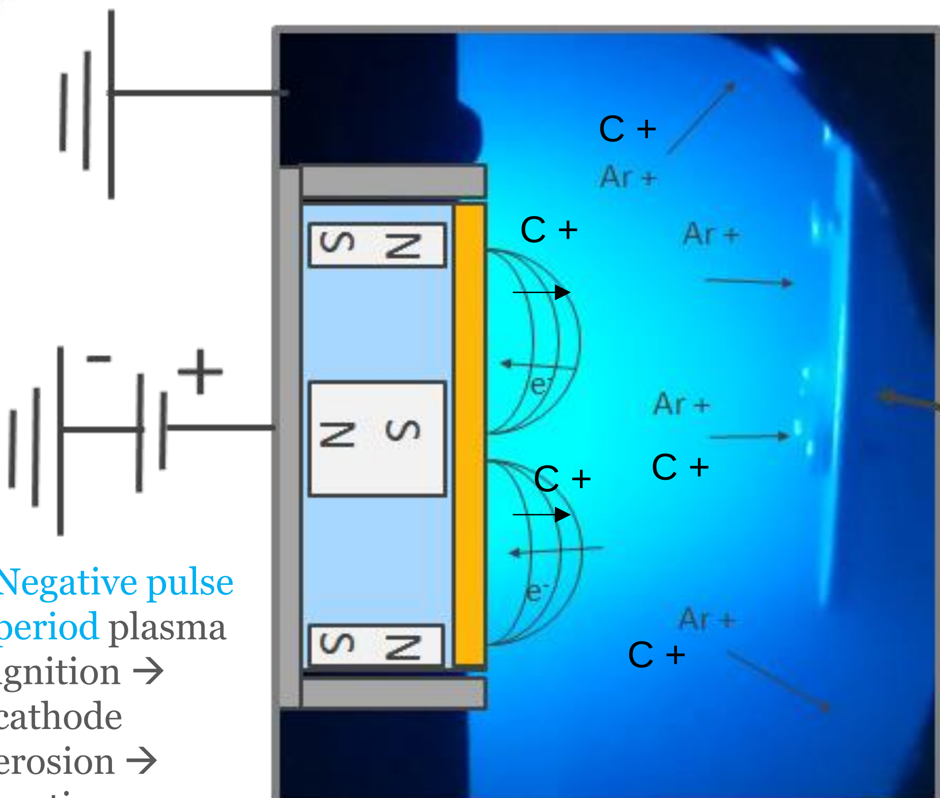
- The sputter deposition of carbon is characterised by a very low sputter rate.
- The two most common allotropic forms of carbon (diamond-like and graphitic) can be deposited, depending of several factors.
- The deposition of diamond-like carbon (DLC) coatings requires some levels of bombardment (ions, electrons) on the substrates. Harder DLC typically requires higher ion bombardment.

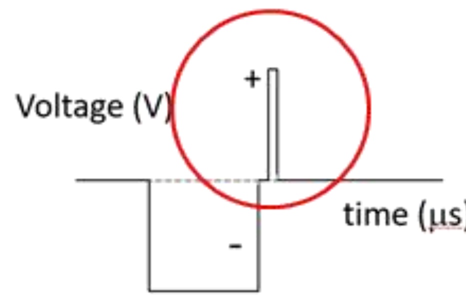
Introduction – Positive bombardment for DLC coatings

- DLC coatings can be produced via PACVD methods from precursors, with the use of ion sources.
- In magnetron sputtering from carbon targets, positive ion bombardment can be ensured by magnetic design (unbalanced) or external elements (e.g. hot filaments, independent ion sources).
- Hard coatings are favoured by the possibility of negatively biasing the substrate
- Ion exposure can be also guaranteed by a control of the plasma discharge.

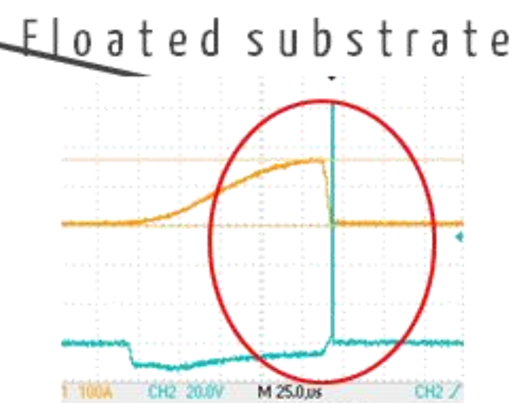
Positive Voltage Reversal Effect

Below is the schematic of the sputter target voltage with a short time +ve pulse (reversed phase) in order to bombard the growing carbon coating





Positive pulse period plasma extinguish → fast plasma potential raise → positive ion acceleration towards grounded substrates



Negative pulse period plasma ignition → cathode erosion → coating deposition

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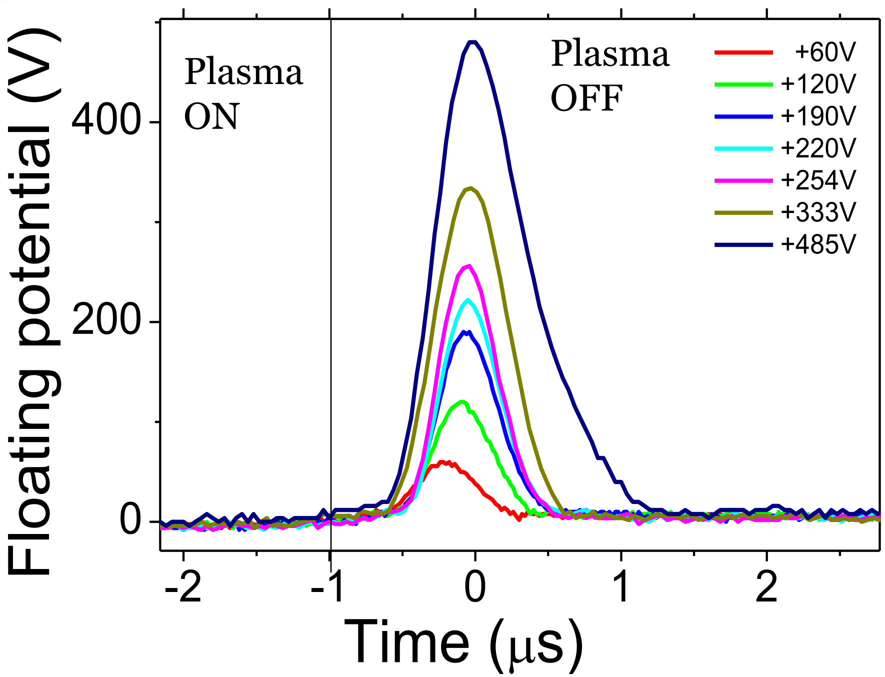
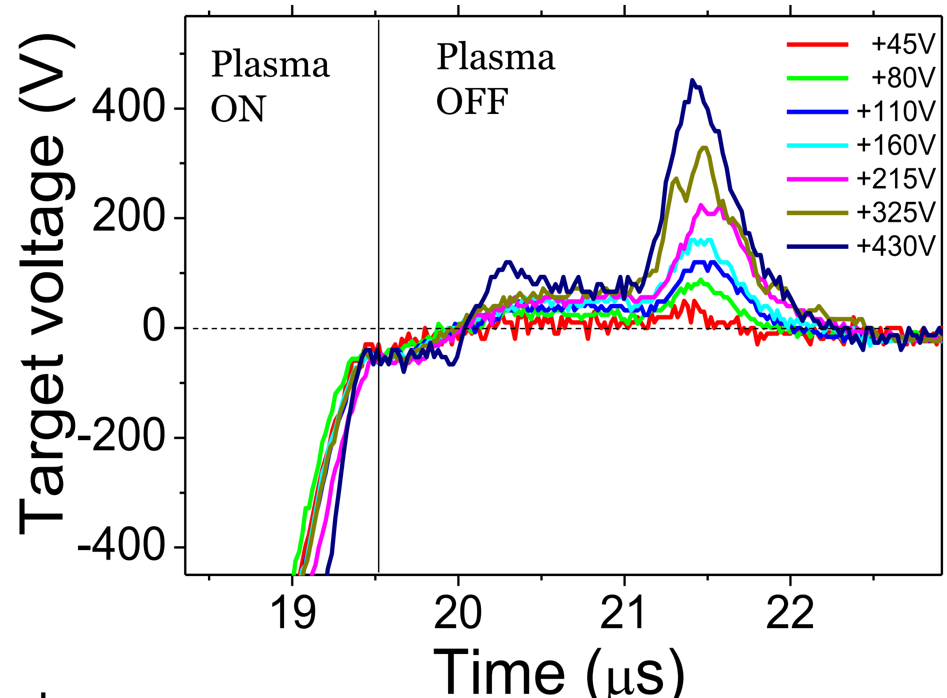
The power supply applies a negative bias to the target to sputter the carbon followed by a positive bias in order to bombard the carbon layer with energetic species and ions





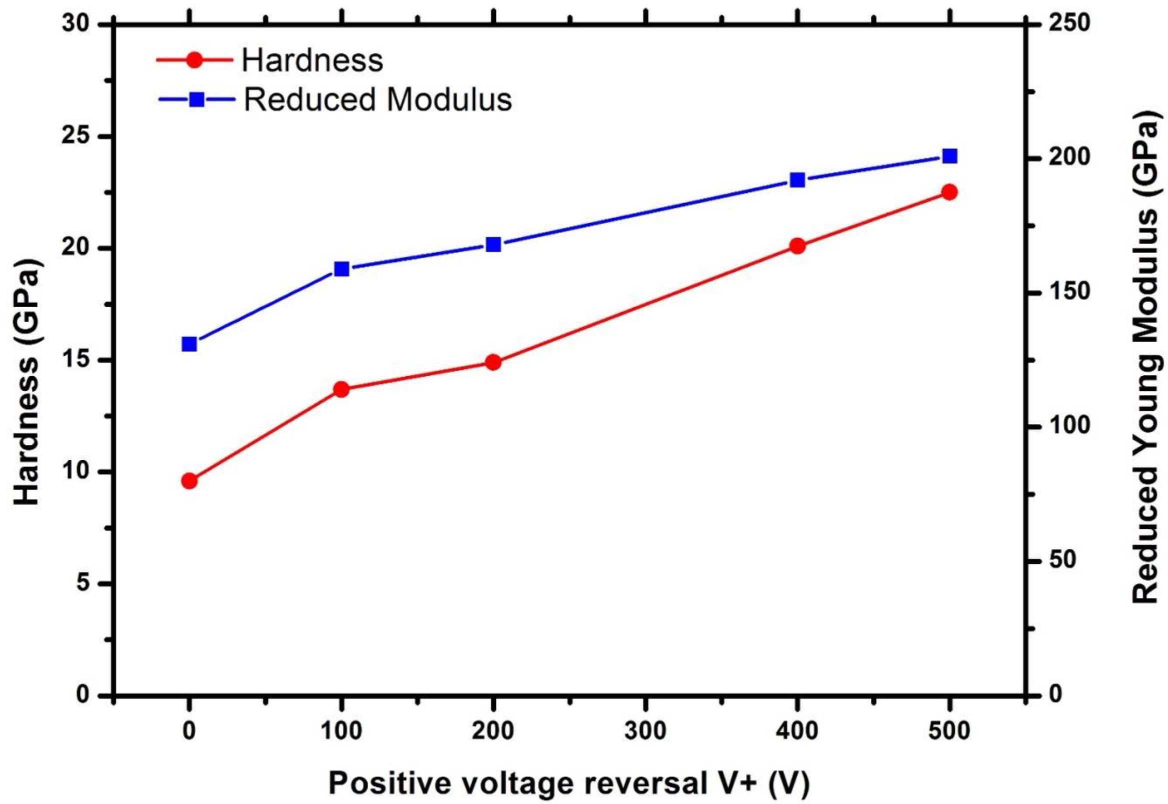
The above floating potential is the substrate potential and assumes about the same level as the target positive reversal voltage

Effect of positive pulse reversal on the hardness of sputtered carbon **on glass**

The hard carbon deposition method uses a positive pulse reversal via the HipV^{+} power supply combined with electron guiding within the sputter chamber - patent pending

The higher the positive pulse, the more the bombardment and the harder the carbon layer

This ‘smart’ ion assistance does not require additional sources

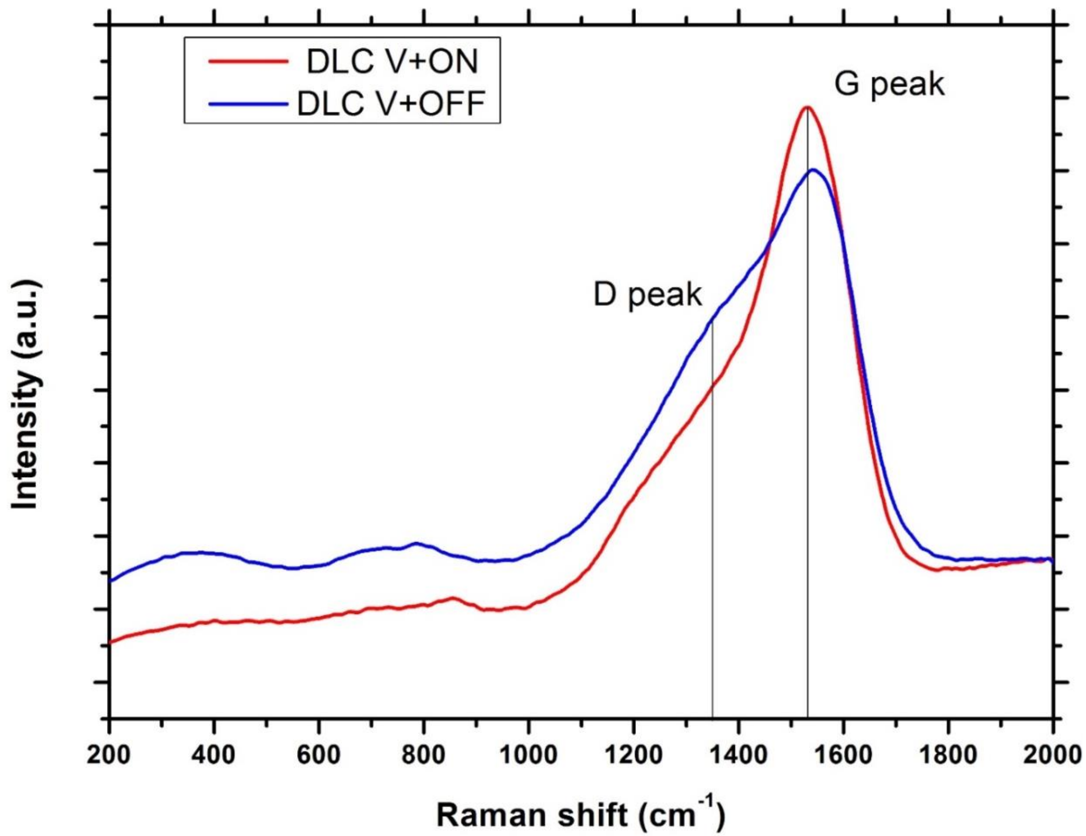


Effect of positive pulse reversal on the sp^2:sp^3 ratio of sputtered carbon

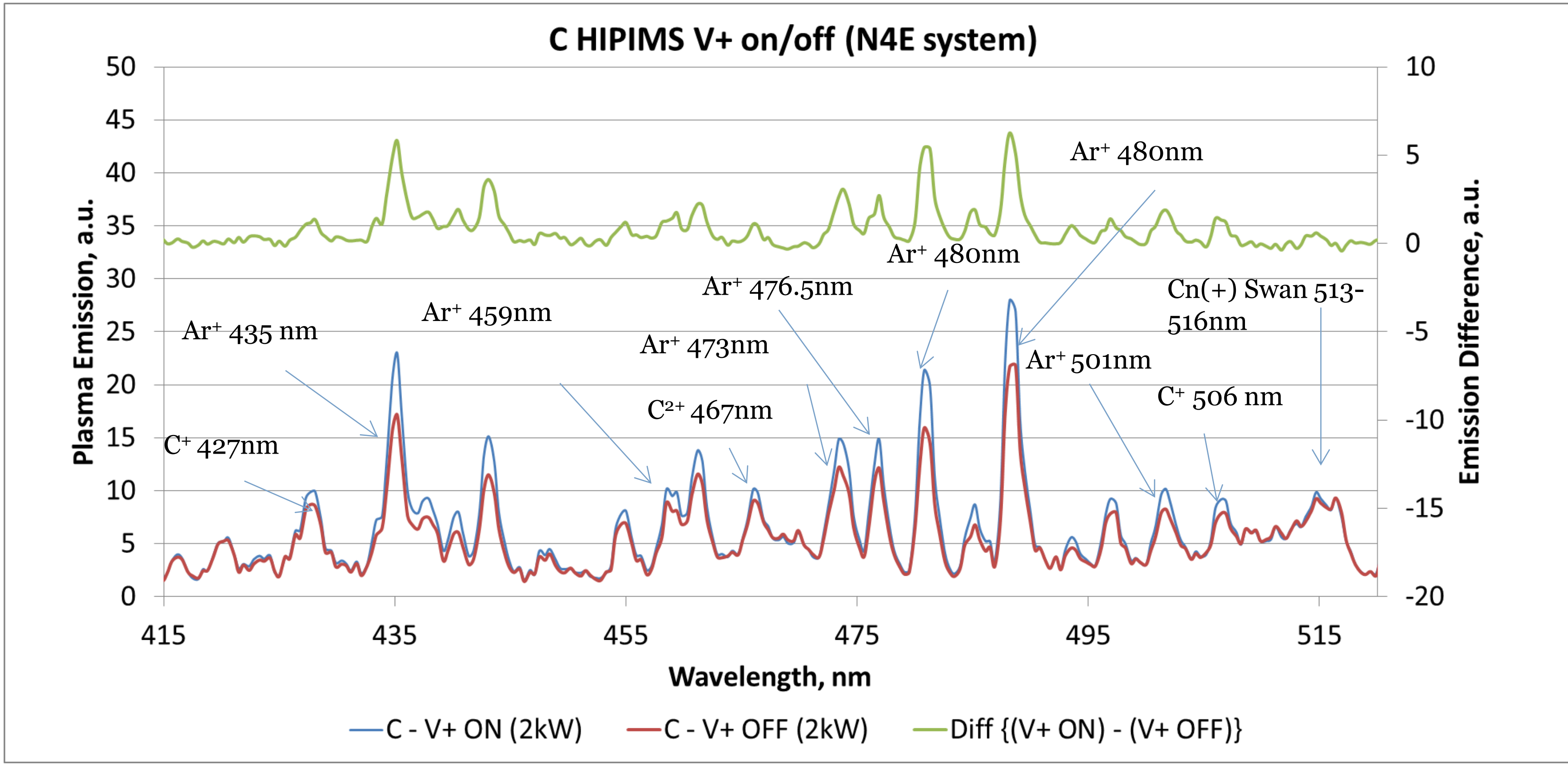
The positive pulse reversal and electron extraction creates an impact of positive ions onto the substrate

This increases the diamond sp^3 type bonding relative to the graphitic sp^2 bonding type

Higher levels of diamond type bonding increases hardness levels



The positive pulse reversal increases ionisation levels within the sputtering plasma as seen in the optical plasma emission spectrum below



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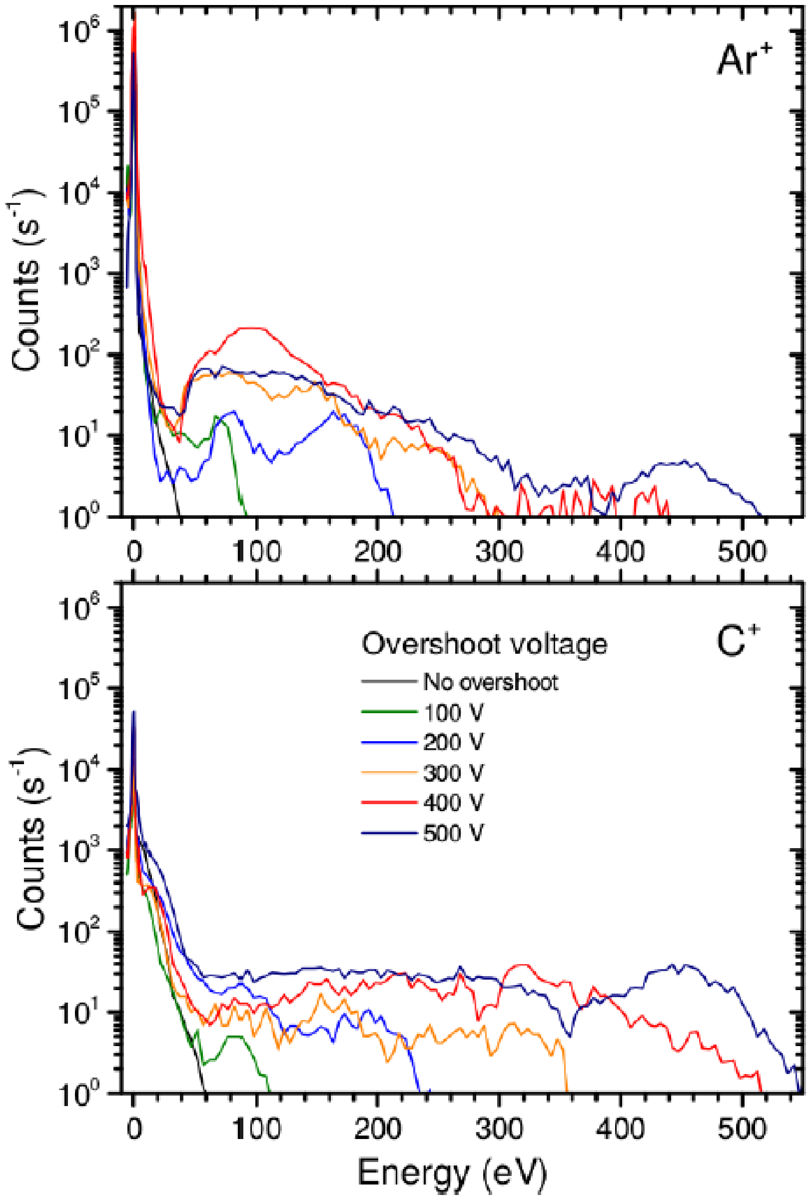
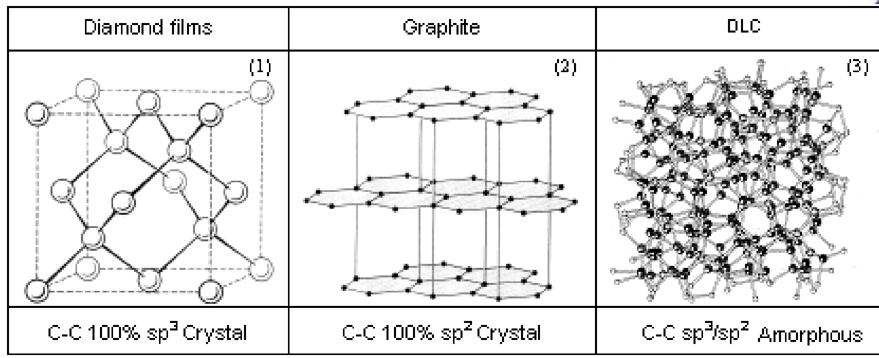
Plasma mass spectrometry



The positive overshoot is key to creating the ions needed to the bombardment of the growing film

The higher the positive overshoot the higher the energy of the ions that impact the growing layer

DLC on glass
Traditional **bias not possible**

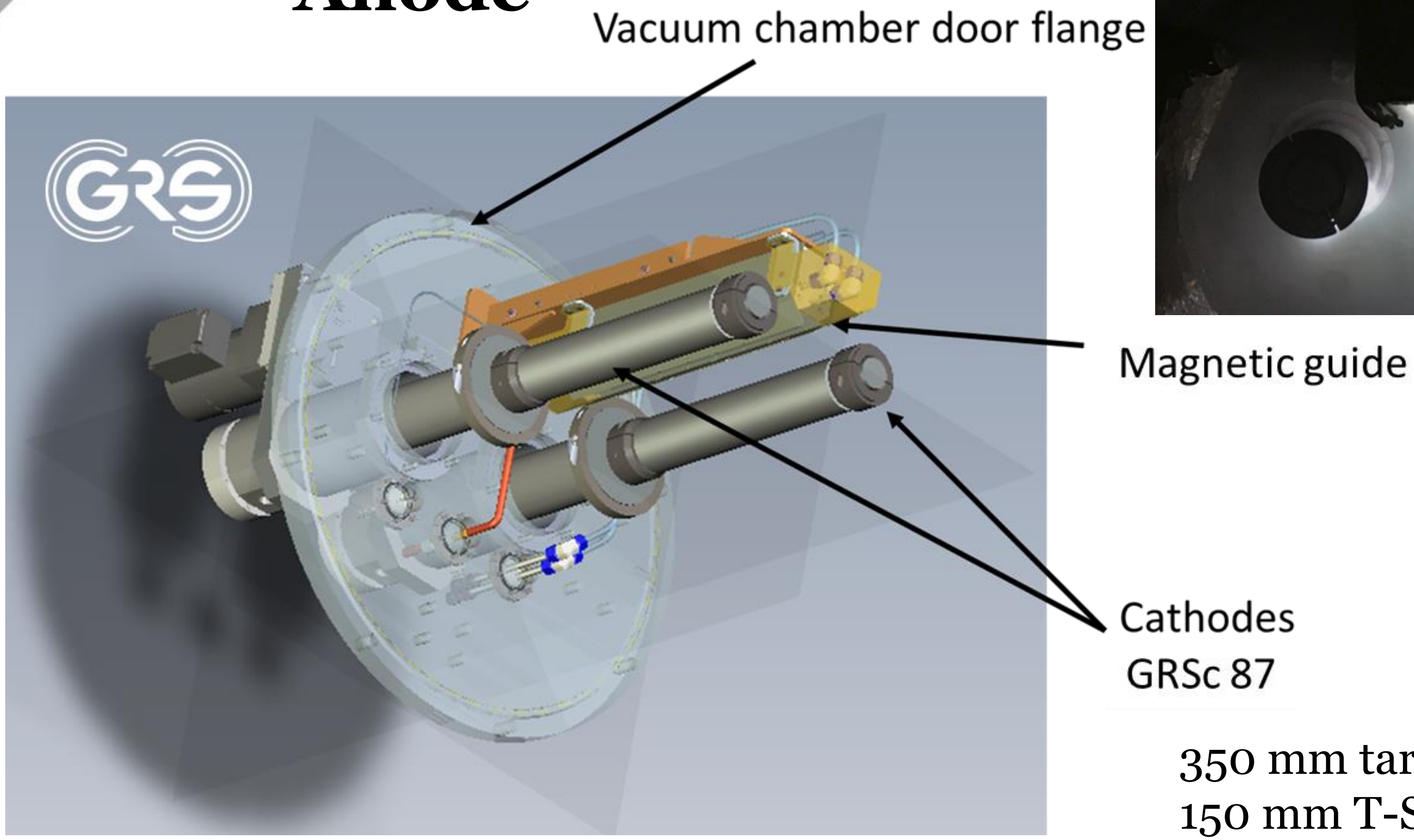


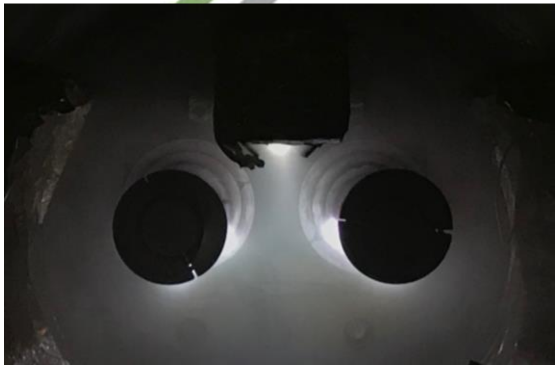
Typical bias on metal substrates enables hardness increase. Glass cannot easily be biased over a large area. The ion energy of impact dominates the hardness

How to take advantage of this new method for abrasion resistant DLC on large area glass?

- Hipims discharges not practical for large area glass – current density too low for Hipims if target is much bigger than 1m in length.
- Rotatable magnetrons most suited to glass coating – carbon is a ‘dirty’ process, hence rotatables best.
- Switching AC or DC bipolar power modes standard in the large area glass industry.
- Hence work has been conducted based upon a dual rotatable with active anode and pulsed DC, AC and bipolar DC switching power to compare the benefits.

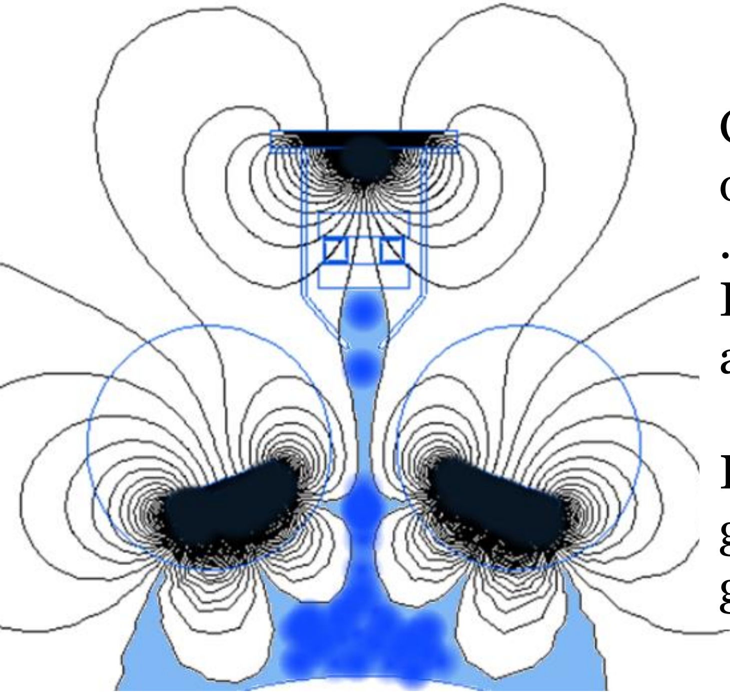
Experimental layout dual magnetron rotatable system – GRS C with Active Anode





350 mm target length
150 mm T-S distance

Importance of electron extraction for hard DLC – Anode magnetic guidance



Gencoa patent for single or dual rotatables

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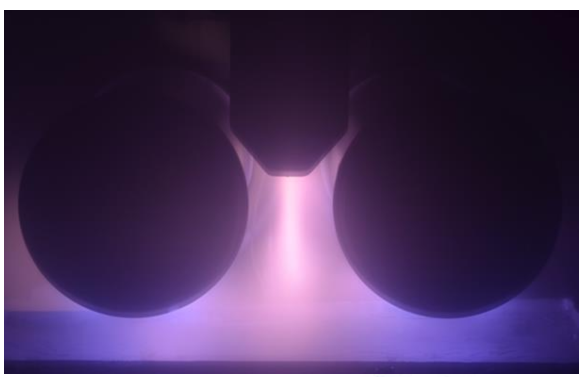
Improves coating density and lowers coating stress.

Essential for hard DLC on glass – otherwise graphitic.

By using the magnetic field design of the magnetron and interaction with other magnetrons or magnetic active anodes, the electron current is separated from the ion current. This increases the impact of the ions and hardens the carbon layer & results in the doubling of the hardness.



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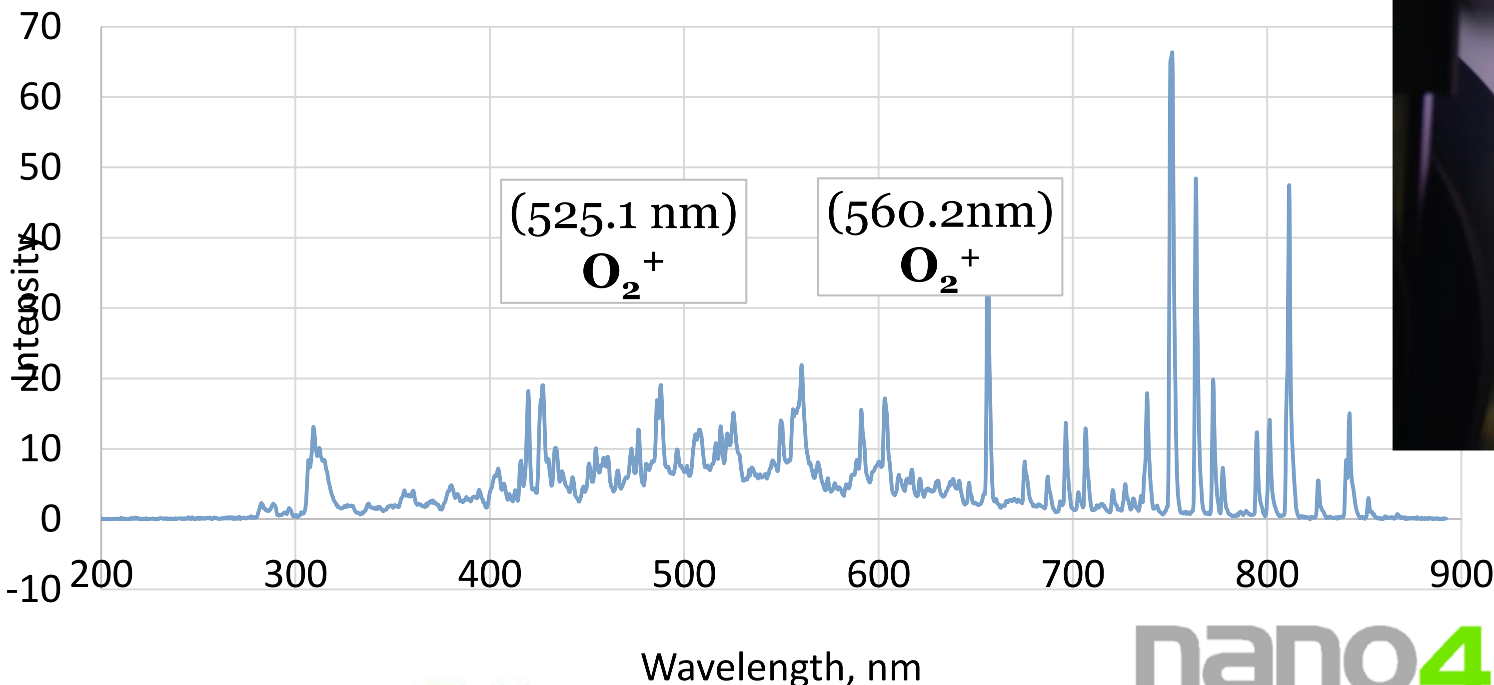
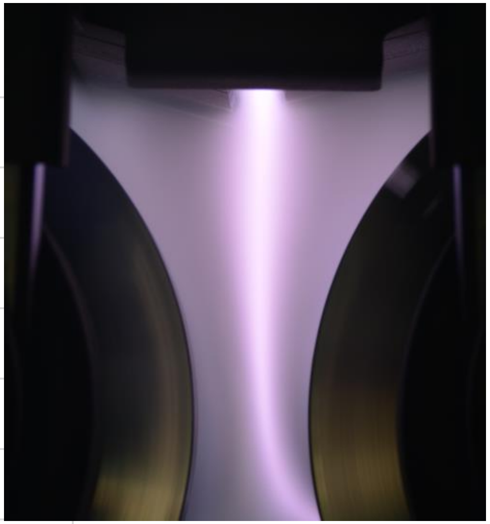
Introducing O_2 through the plasma in the anode zone increases the V(+) pulse intensity and produces higher O_2^+ ionization

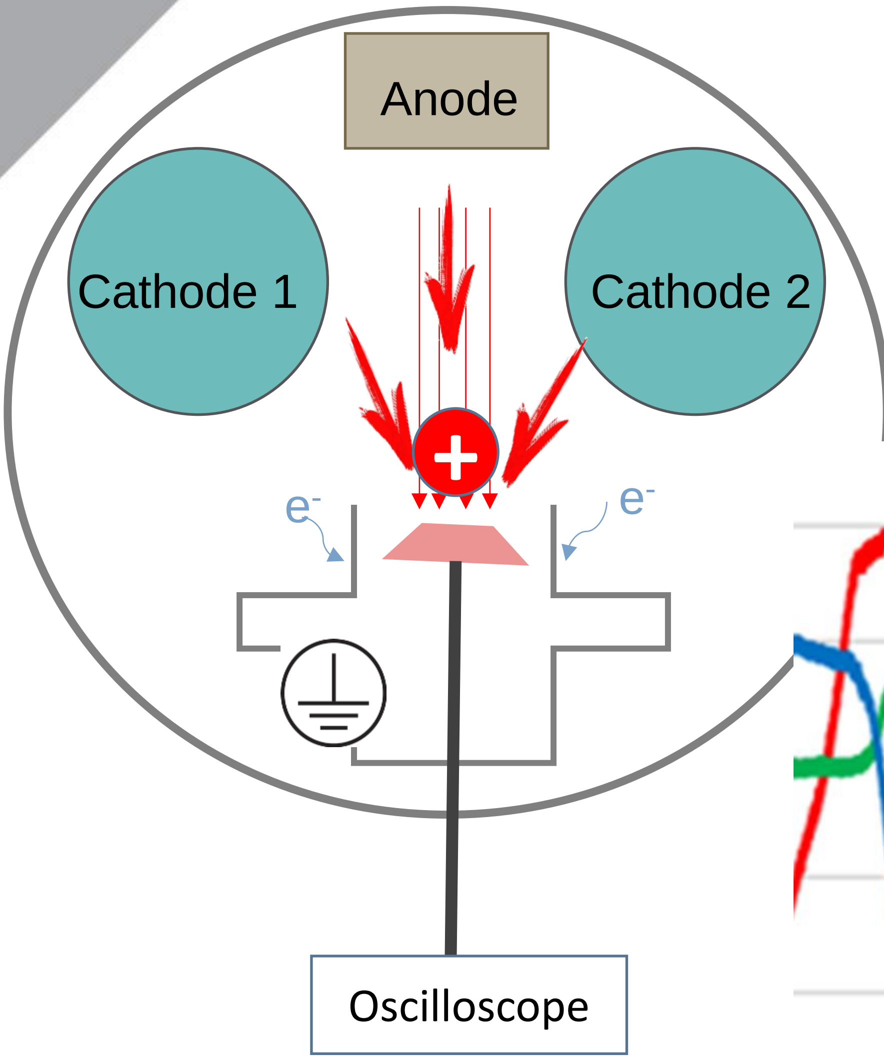
This method is used for pre-cleaning glass before DLC coating

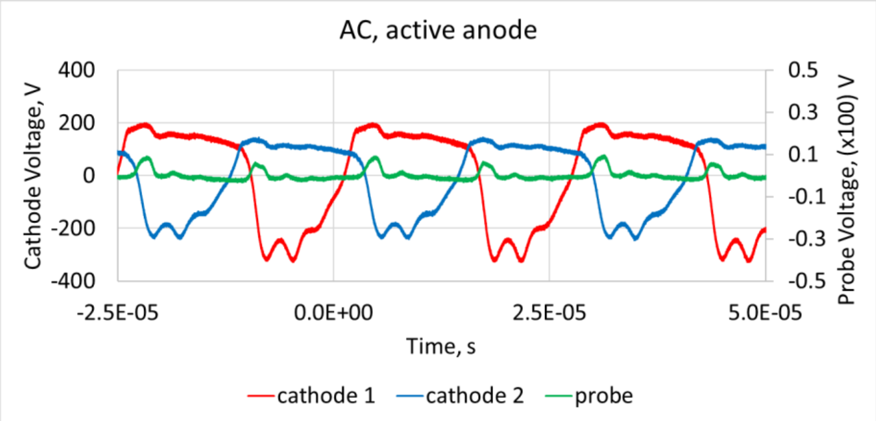
Can be used for large area glass cleaning in general – 2 x carbon targets, AA and Ar/O_2 gas mix with AC or switching power

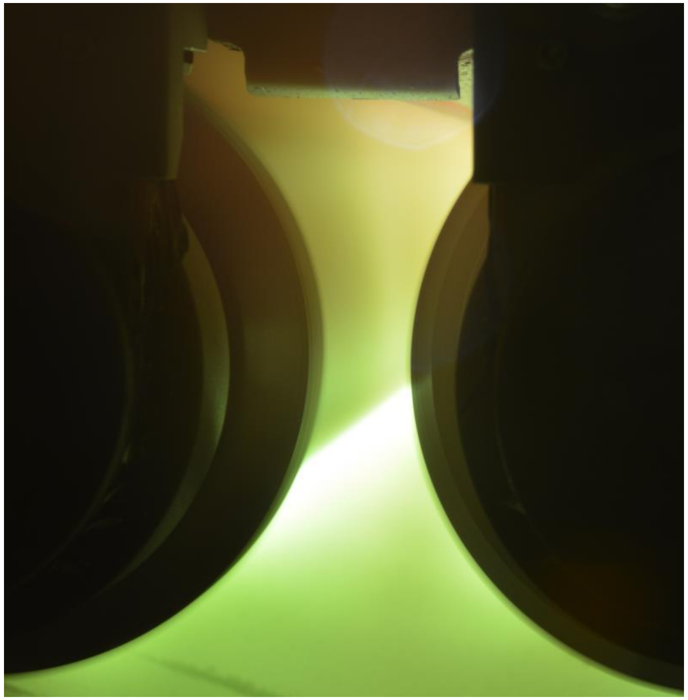




Active anode and AC power mode produces the positive Ar and O2 bombardment

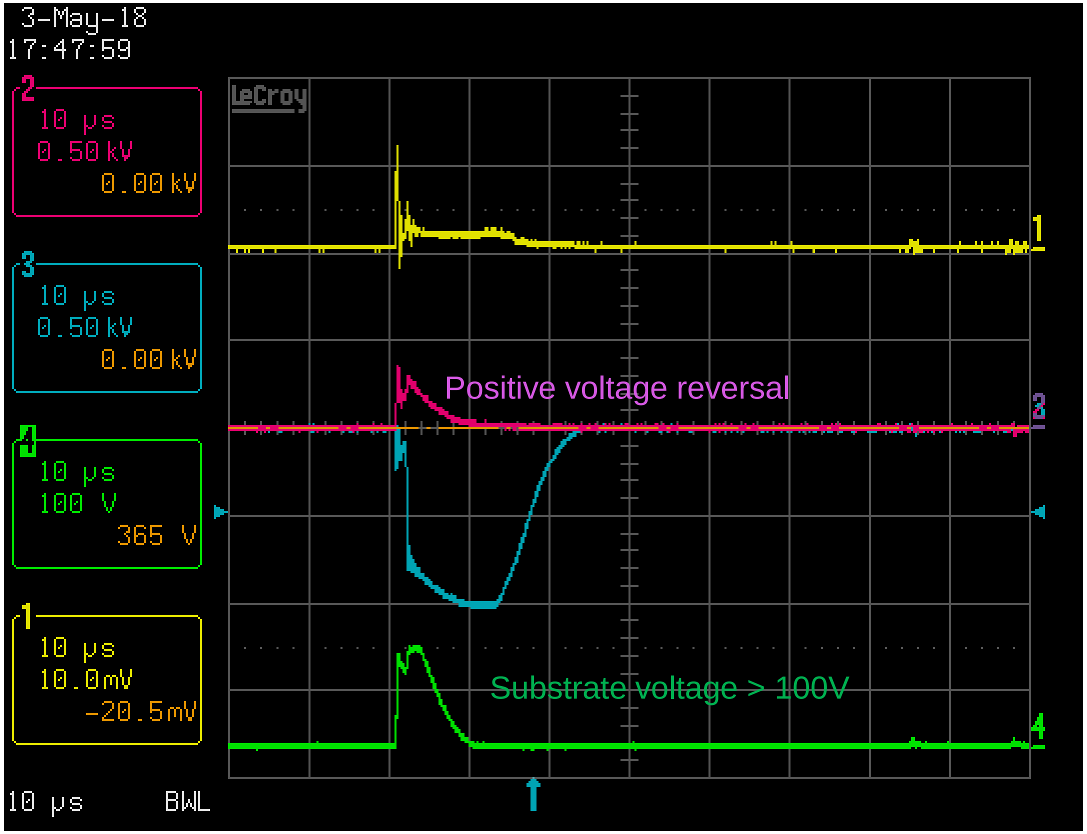


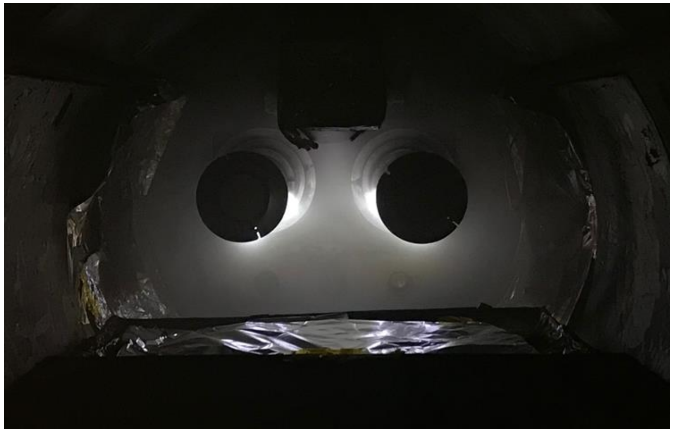




Dual rotatable GRSC & AA – with HIPIMS discharge – N4E Power Supply

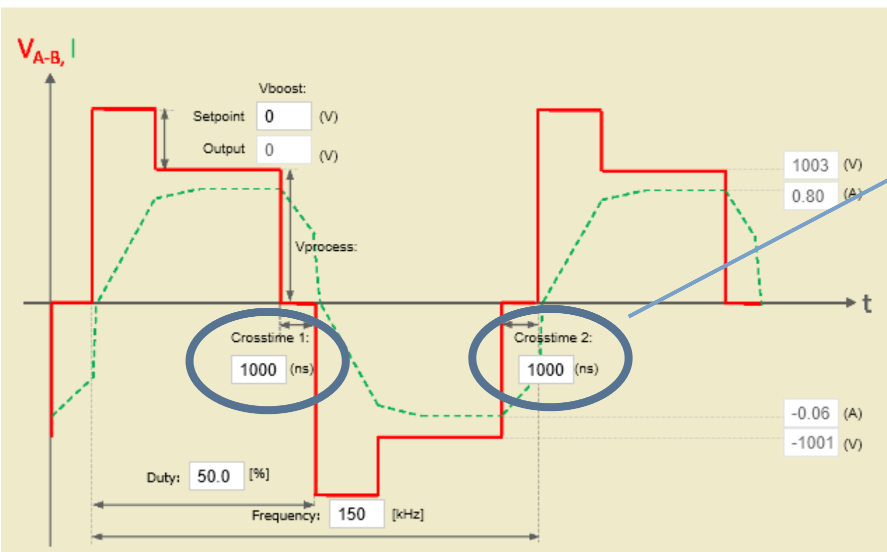
Cathode voltage reversal > 100 V biasing on the substrate area





For large area glass AC or bipolar DC most suited - switching delays option

- A tweaked square-wave bipolar generator (AE Ascent DMS) is used for maximising a positive peak bias on the target surface, able to propel ions towards the sample

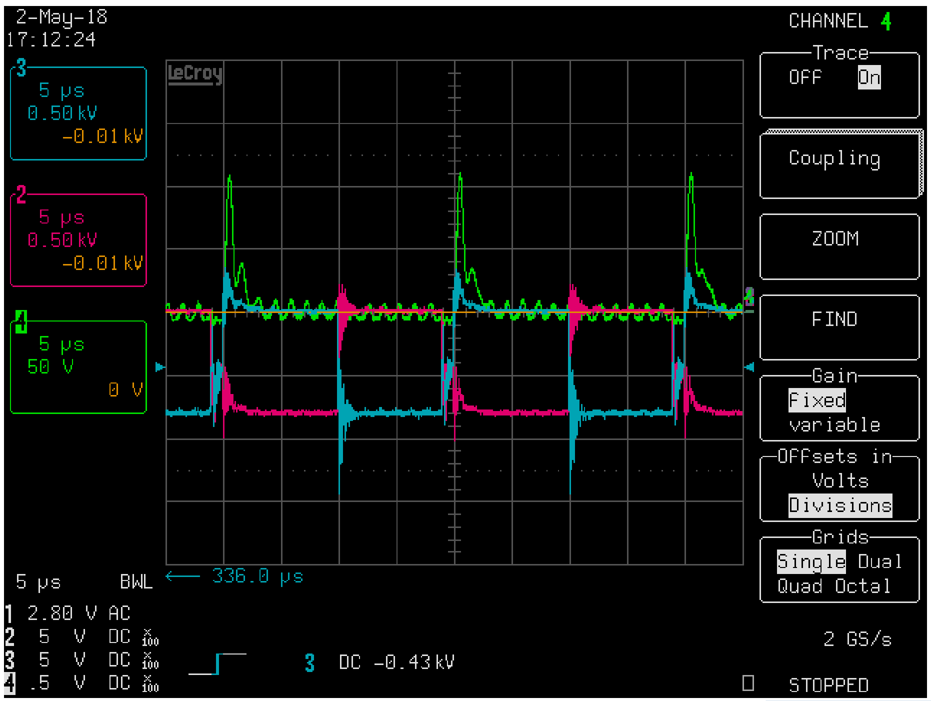


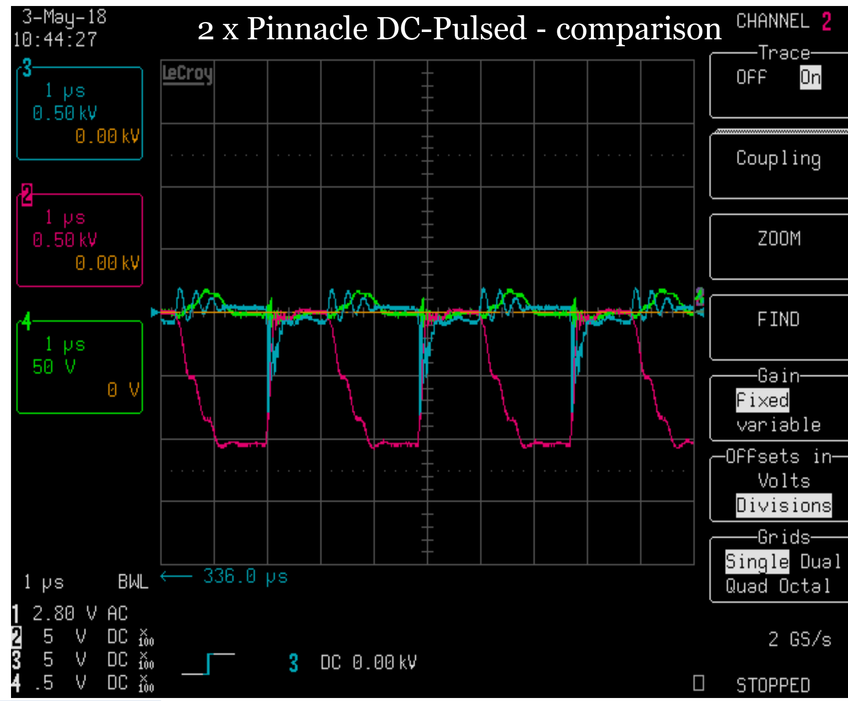
The cross-time or delay is the time off and can be set (max 1 μs) within the duty cycle (max 2 delays per period)

During this time power is off. It affects the square-wave discharge inducing a sensibly higher peak-to-peak voltage

Dual bipolar discharge

Ion bombardment can be adjusted by inserting a delay after each cycle

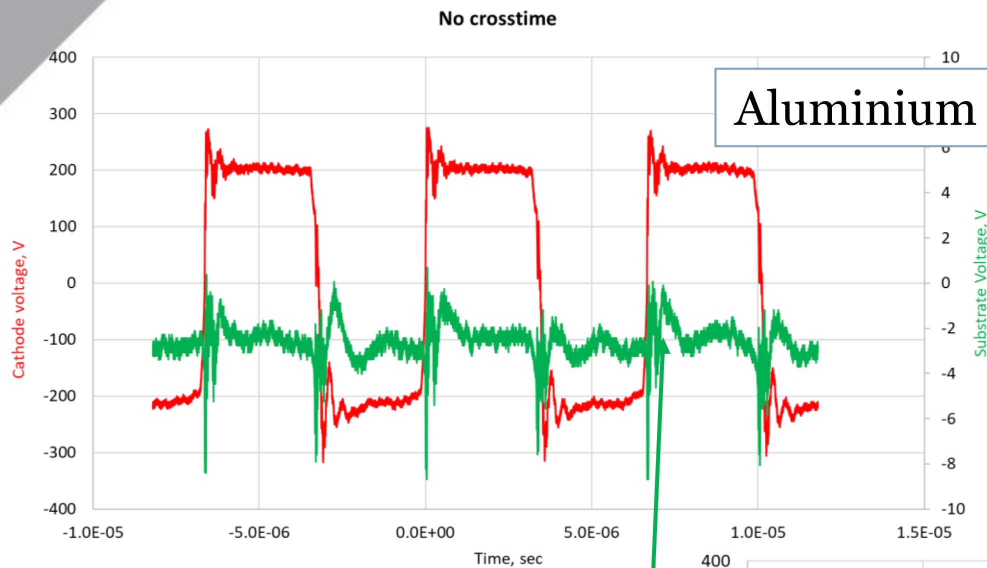




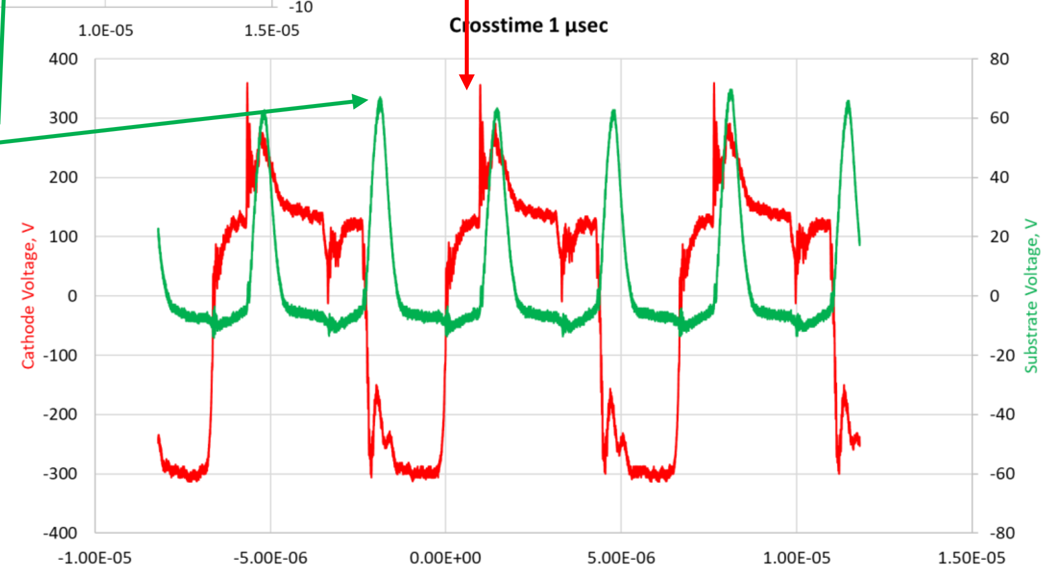
Carbon targets

Positive bombardment with and without switching delay

Aluminium targets, excess of O_2



When cross-time is active, positive peak is boosted



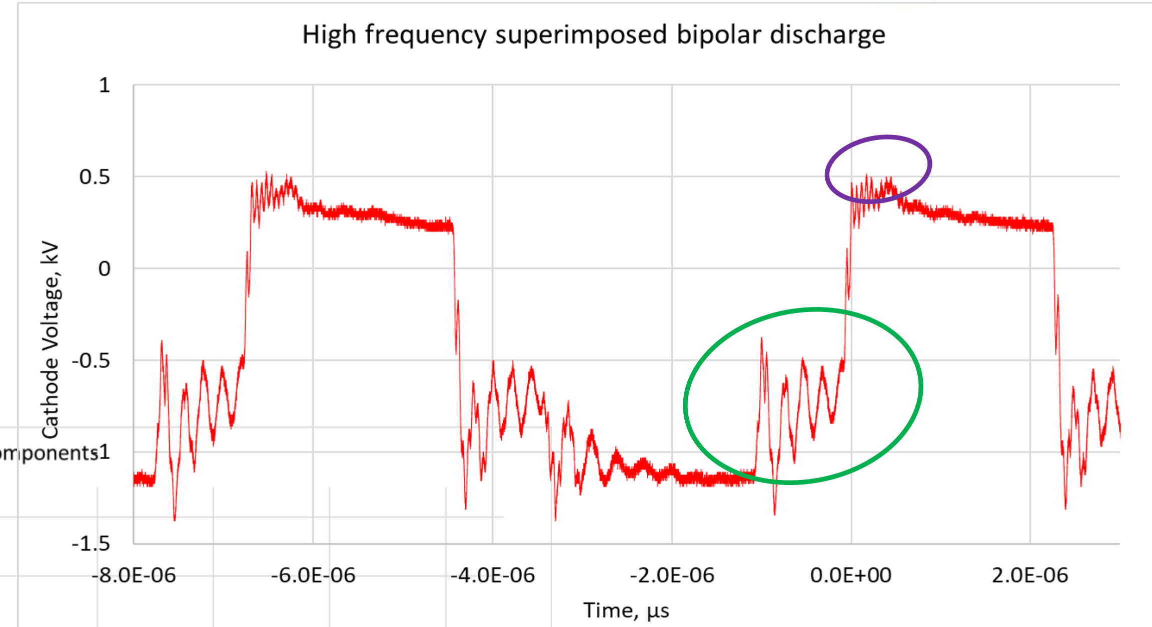
A positive bombardment on the substrate region is also measured

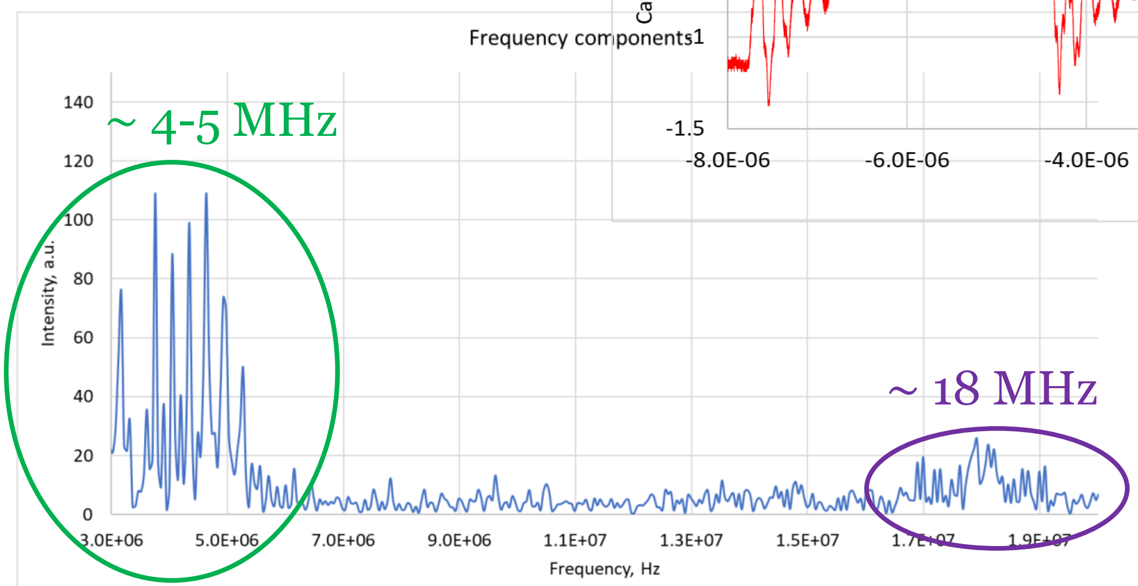
(After the cross-time, ions in the system are accelerated away by the positive magnetron)

Enhanced peak-to-peak voltage + high frequency discharge

Main frequency is 150 kHz

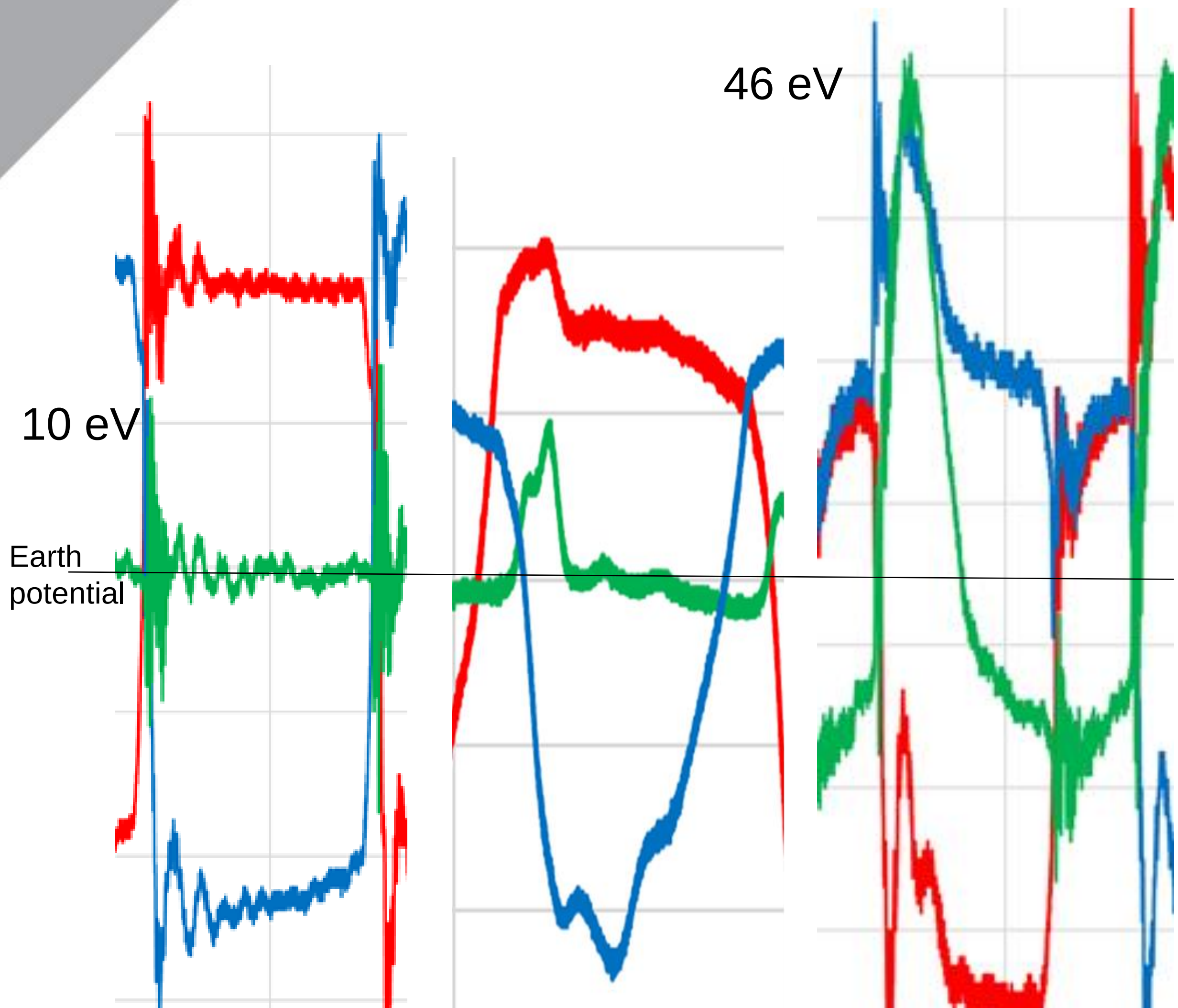
DFT analysis of the discharge





High-frequency components are observed. These can play a role in ionisation enhancement

The Active Anode will create positive bombardment with all power modes – DC pulsed, AC, Hipims, DC Bipolar



Standard square wave switching with Active Anode

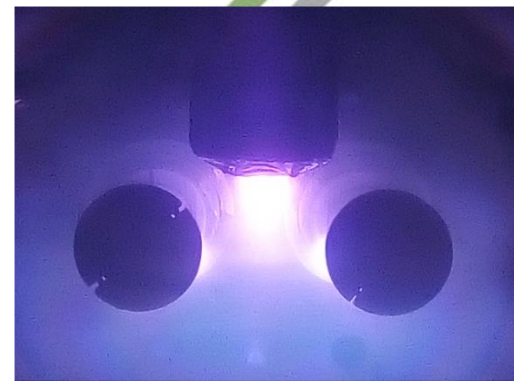
Standard AC power with Active Anode

Square wave switching with 1μsec delay and Active Anode

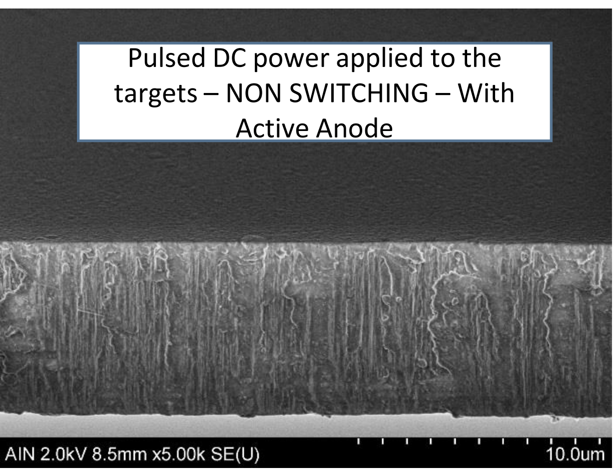
- By switching electrons between targets extra ionisation is created
- Active Anodes AA creates positive and negative energy bursts on the substrate (ideal for glass or plastic substrates without external bias)
- Different levels depending upon power mode
- Introduction of a delay in the power switching increases positive energy

Creation of extra energy via power mode and Active Anode – comparison of coating structures

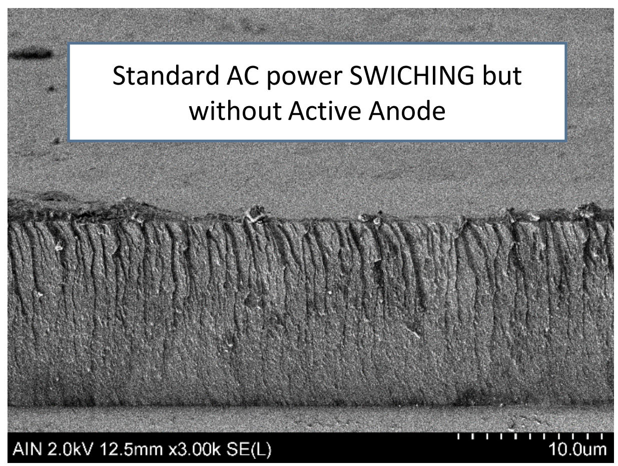
10 micron thick AlOx deposited onto glass (floating potential – no external bias) from a dual rotatable magnetron and with active anode



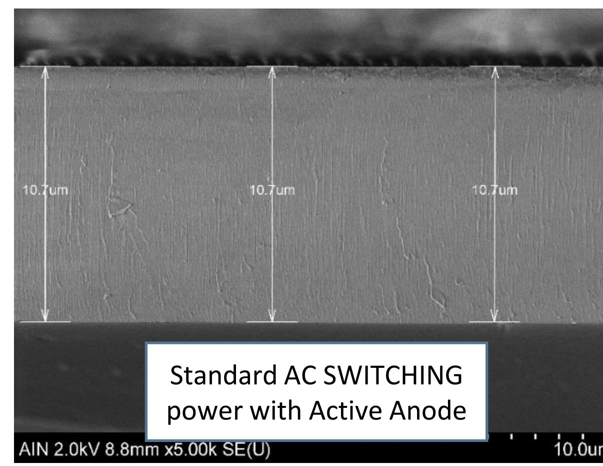
Increasing Energy Levels



Columnar structures are recurrent when DC-Pulsed is used

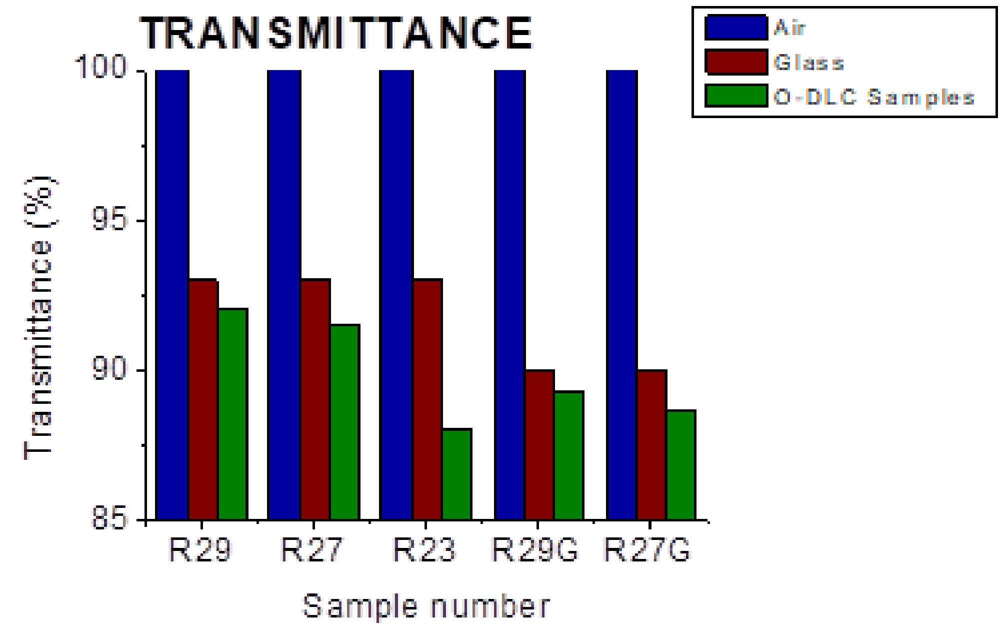


AC switching power mode has improved structure compared to pulsed DC

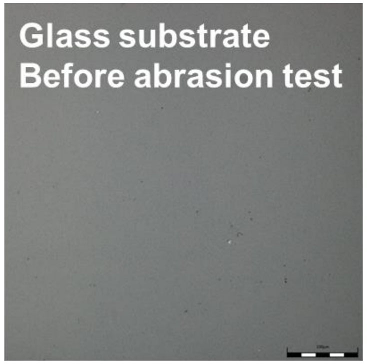


AC with active anode Produces highly dense structure

DLC by this method is highly transparent – just 1% loss



SAMPLE	Sample Transmittance (%)	Glass Transmittance (%)	$\Delta T_{DLC} = T_{glass} - T_{DLC}$ (%)
Air	100	-	-
R29 (10 nm)	92.0	93	1.0
R27 (15 nm)	91.5	93	1.5
R23 (125 nm)	88.0	93	5.0
R29G Thick glass(10 nm)	89.2	90	0.8
R27G Thick glass (15 nm)	88.6	90	1.4

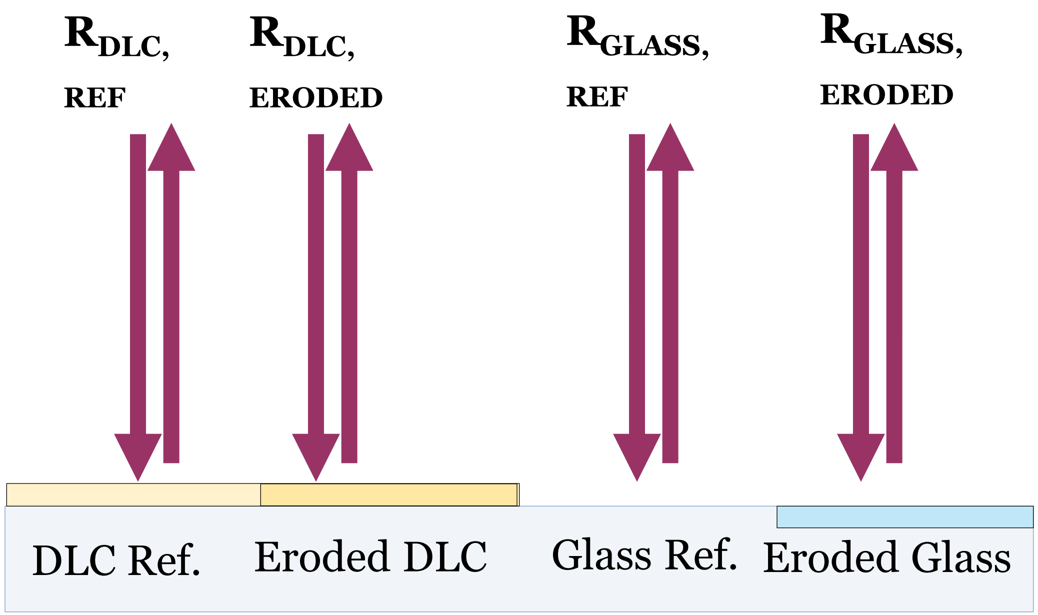


2-5nm thick V±EE DLC on glass : Specular reflectance after abrasion tests

$\Delta R_{DLC} = R_{DLC,\ ERODED} / R_{DLC,\ REF} \sim$ 5-10%

$\Delta R_{GLASS} = R_{GLASS,\ ERODED} / R_{GLASS,\ REF} \sim$ 20-25%

The samples are subject to 5 minutes sand oscillation test with silica sand



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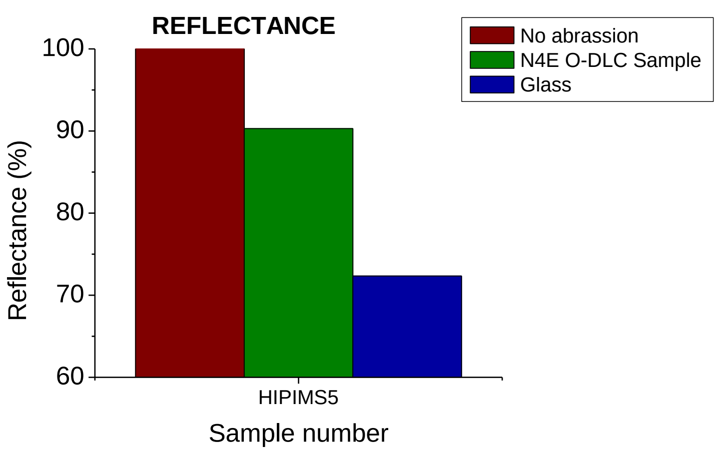
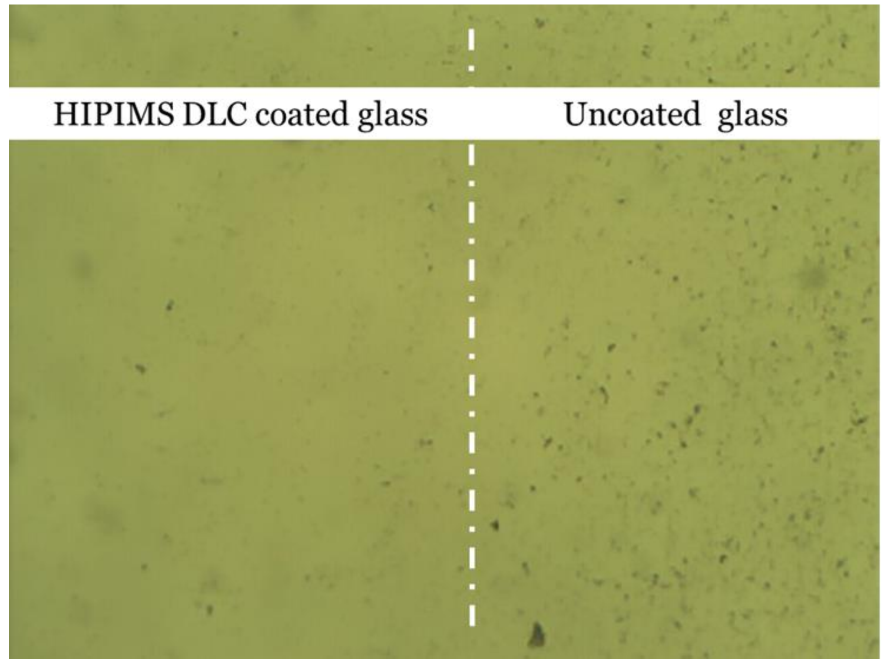
Abrasion tests DLC on glass

100x objective
Deuterium + halogen lamp
SpeedFlo CCD Spectrometer





After 5 min abrasion test x 10 magnification

SAMPLE	$R_{DLC, ERODED}$ / $R_{DLC, REF}$ (%)	$R_{GLASS, ERODED}$ / $R_{GLASS, REF}$ (%)	DLC Coating Improvement (%)
HIPIMS5 (5 nm)	90.3	72.3	18.0

* 5 minutes abrasion with "Sand oscillating test" using Silica Sand

Optical DLC just 2 to 5nm thick provides scratch and abrasion resistance compared to uncoated

Sample Name	Thickness (nm)	Coating Transmittance (%)	$100 - \frac{R_{Coat,eroded}}{R_{coat,ref}}$ (%)	$100 - \frac{R_{Glass,eroded}}{R_{Glass,ref}}$ (%)	DLC Coating Improvement (%)
HIPIMS_5	5	87.2	9.7	27.7	18.0
HIPIMS_4	3.5	86.1	4.5	13.7	9.2
HIPIMS_6	2.8	86.3	1.4	7.8	6.4
HIPIMS_3	2.1	89.6	4.9	14.0	9.1
HIPIMS_7	3.5	90.3	3.3	15.3	12.0
HIPIMS_8	3.5	90.6	5.0	8.2	3.2
HIPIMS_9	3.5	90.8	2.9	19.0	16.1

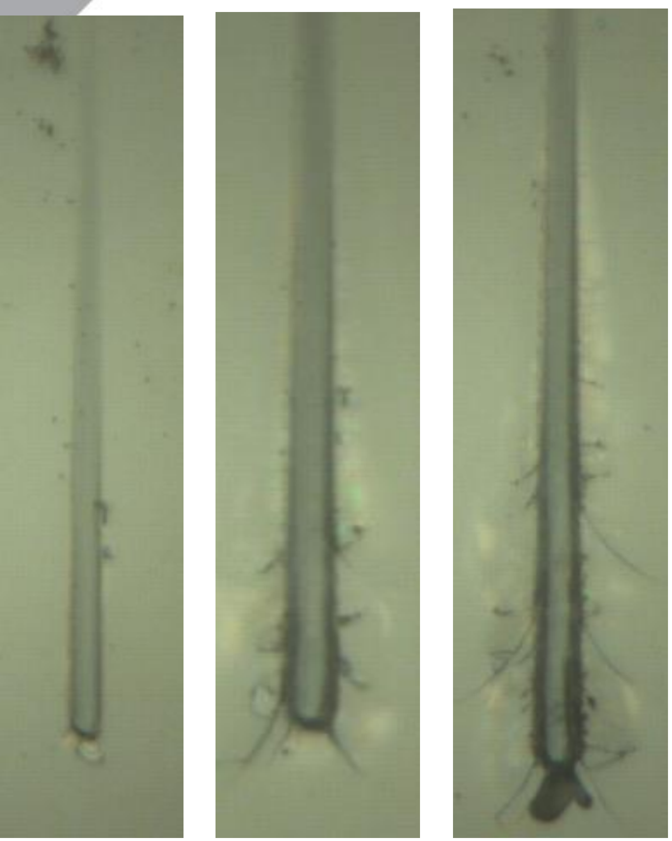
Microscractch tests on DLC coated glass

Conditions

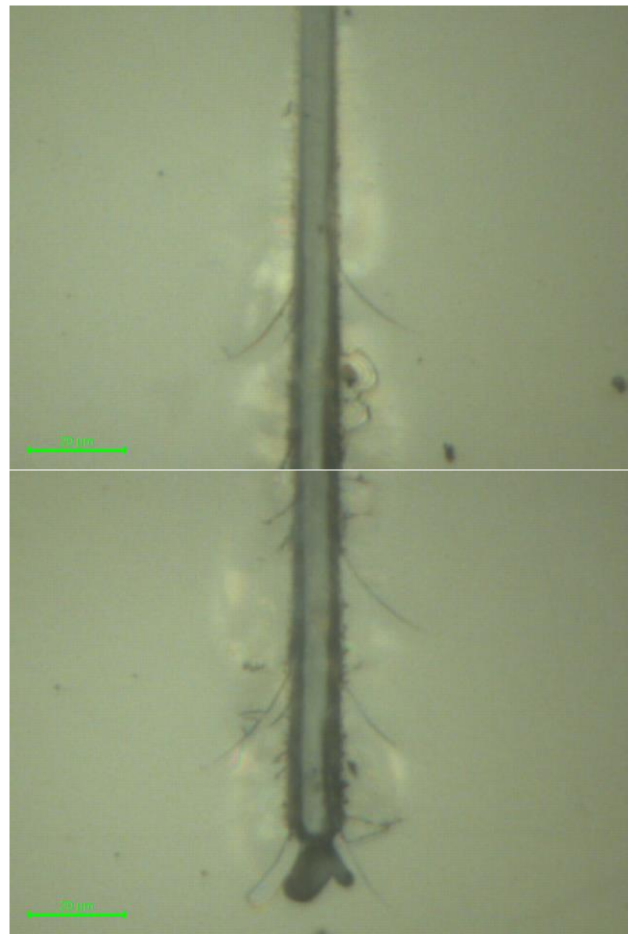
- Sphero-conical tip with a **tip radius** of 10 μm
- **Load rate** was 0.75 (mN/μm) for thicker films (350nm) and it was reduced to 0.33 (mN/μm) for under 100 nm films
- **Maximum** normal **load**: 500mN
- Scratch **length**: 300 μm
- 5 scratches in each sample
- All scratches were done at 1 mm away from one of the edges (to keep the rest of the sample clean for future experiments)
- Different **failure modes** for each sample

Microscractch tests on DLC coated glass

DLC_Cal_5



Scratch tracks (300, 400, 500 mN)



Critical load: ≈ 300 (mN)

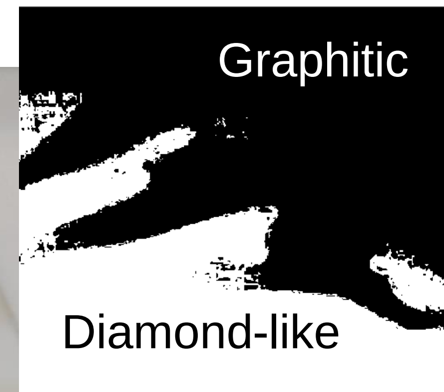
Very good adhesion – O2 plasma pre-clean

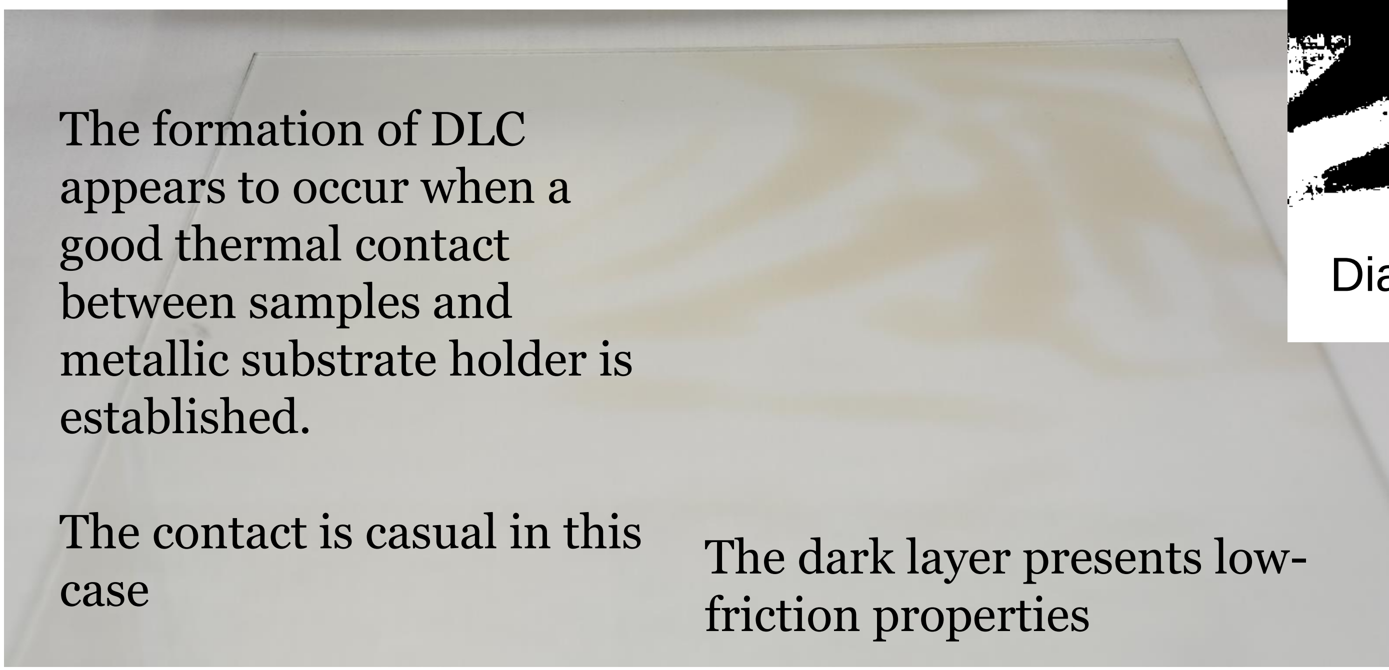
Delamination failure

>8 Mohr hardness for 3nm thick DLC

Temperature effect

If the glass is too hot, then graphitic rather than diamond like material will be deposited. Graphitic carbon, which appears darker, is thermodynamically more stable and is favoured at> 150 ^{0}C.





The formation of DLC appears to occur when a good thermal contact between samples and metallic substrate holder is established.

The contact is casual in this case

The dark layer presents low-friction properties

Conclusions

- Hard, transparent and abrasion resistant DLC can be deposited on floating substrate as a result of combined positive voltage reversal on the target and electron extraction sputtering.
- This is achievable both with HIPIMS, AC, pulsed DC and dual bipolar power modes on planar or rotatable sources.
- The presence of a magnetic guidance of electrons away from the substrate is required for high ion bombardment.
- The hardware and power supplies are readily available to allow optical DLC on large area glass.
- The same arrangement can be used for plasma cleaning of glass via the use of Oxygen and carbon targets.
- The technology is already being used for the production of scratch resistant layers on glass.

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