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State-of-the-Art of DLC Coatings: Industrial Deposition Methods and tribological Applications 60 Years after the Discovery of DLC

J. Vetter, C. Ackermann, M. Fromme, F. Meunier; O. Jarry, G. Erkens, Mai, 01, 2013

HALL OF FAME

1. DLC „an accidental discovery“

2. Enormous property and application field

3. Cathodic vacuum arc: a-C/ta-C

4. PACVD: a-C:H:X
   Ion- and plasma sources
   Glow discharges (RF and DC/AC pulsed)

5. Sputtering of a-C, a-C:H:Me and more

6. Hybrid processes PVD plus PACVD

7. Summary and outlook

and many others …

1953 – 2013: 60 years DLC

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DLC: first time – a kind of accidental discovery

Schmellenmeier: *I want to carburize galvanized W/Co coatings to make „widea“ surfaces (cemented carbide) for wear protection - for example on HSS drills*

Prof. Dr.
H. Schmellenmeier
Inst. Exp. Physics
Univ. of Education
Potsdam/Germany

EXPERIMENTELLE TECHNIK DER PHYSIK
HERAUSGEGEBEN VON F. X. EDER UND A. ECKARDT
1. JAHRGANG SEPTEMBER 1953 HEFT 2

ORIGINALARBEITEN

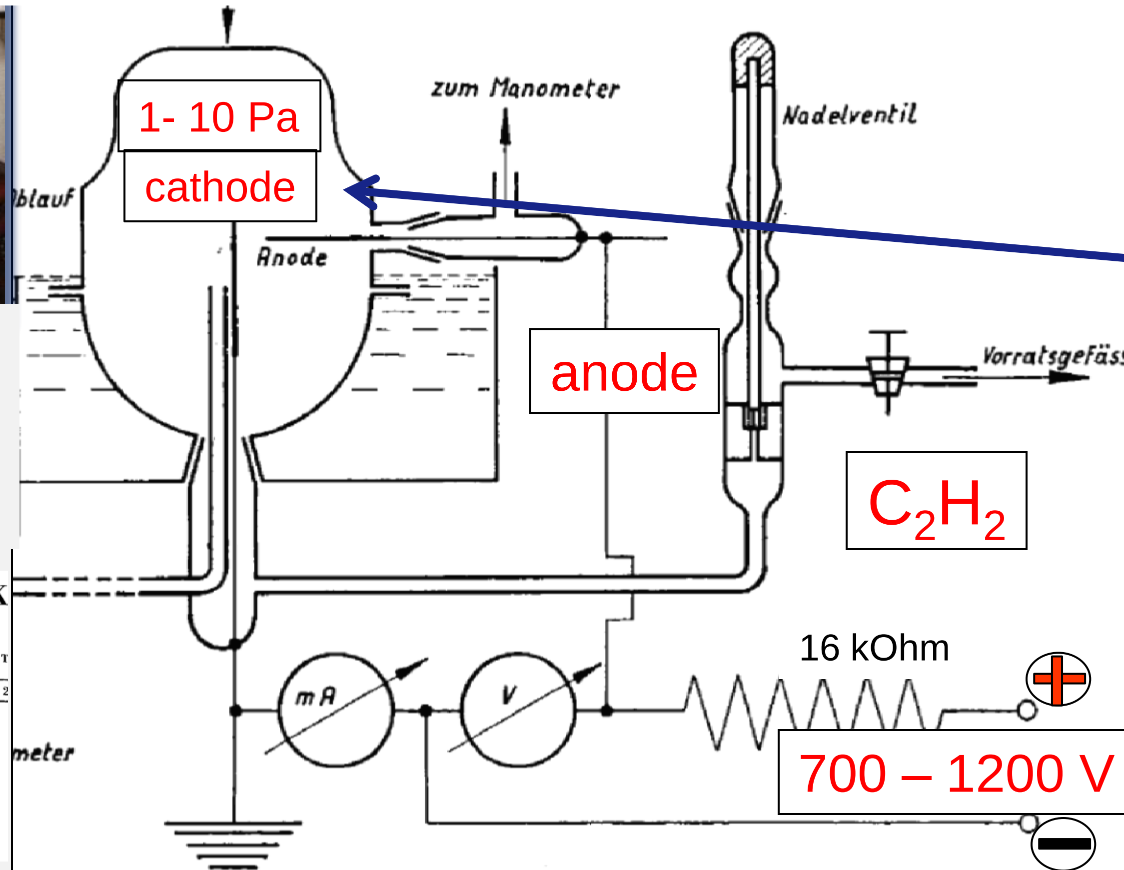
Die Beeinflussung von festen Oberflächen durch eine ionisierte Gasatmosphäre

I. Die Reaktion zwischen Wolfram und Kohlenstoff

von Heinz Schmellenmeier, Potsdam

Im Auszug vorgetragen auf der Tagung „Gasentladungsphysik“ der Physikalischen Gesellschaft der DDR, Halle, 3.—5. September 1953

(Eingegangen am 20. 1. 1953)



Substrates:

galvanic W/Co coated

- steel plates
- drills

Wow !!!! Whats wrong? ***A black bright coating!***

Lets have a look!

The first described a-C:H coating was born! 1953

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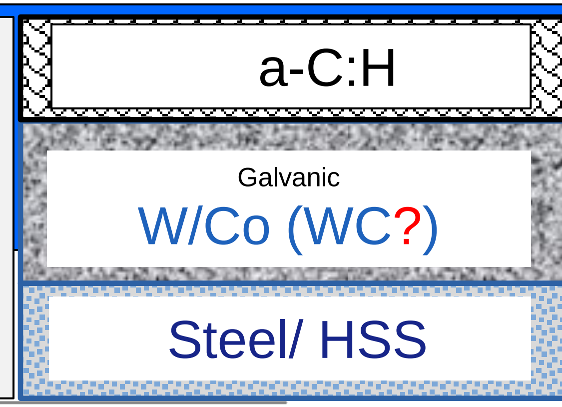
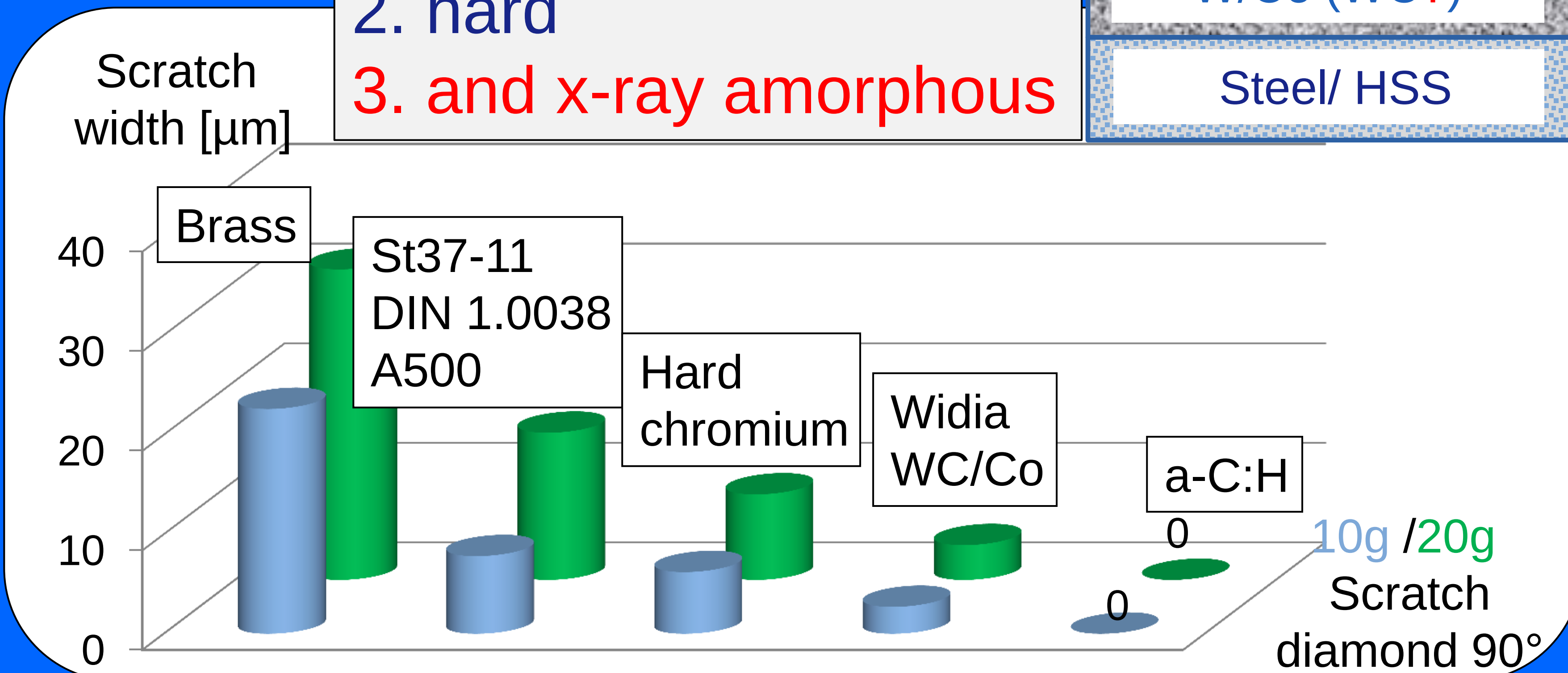
black bright coating:
1. scratch resistant
2. hard
3. and x-ray amorphous





The potential of a-C:H as tribological coatings was shown in 1953!
Thats the main content of my talk.

Applications of DLC 1: DATA STORAGE
Hard disks and optical storage divices (blueray)

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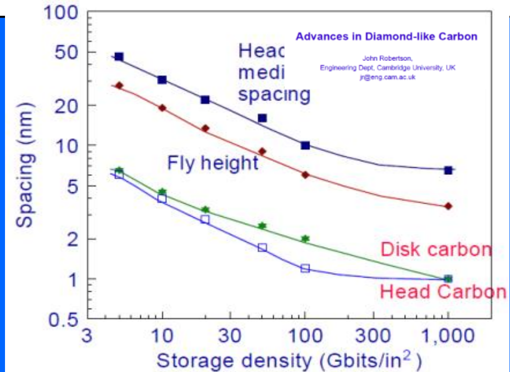
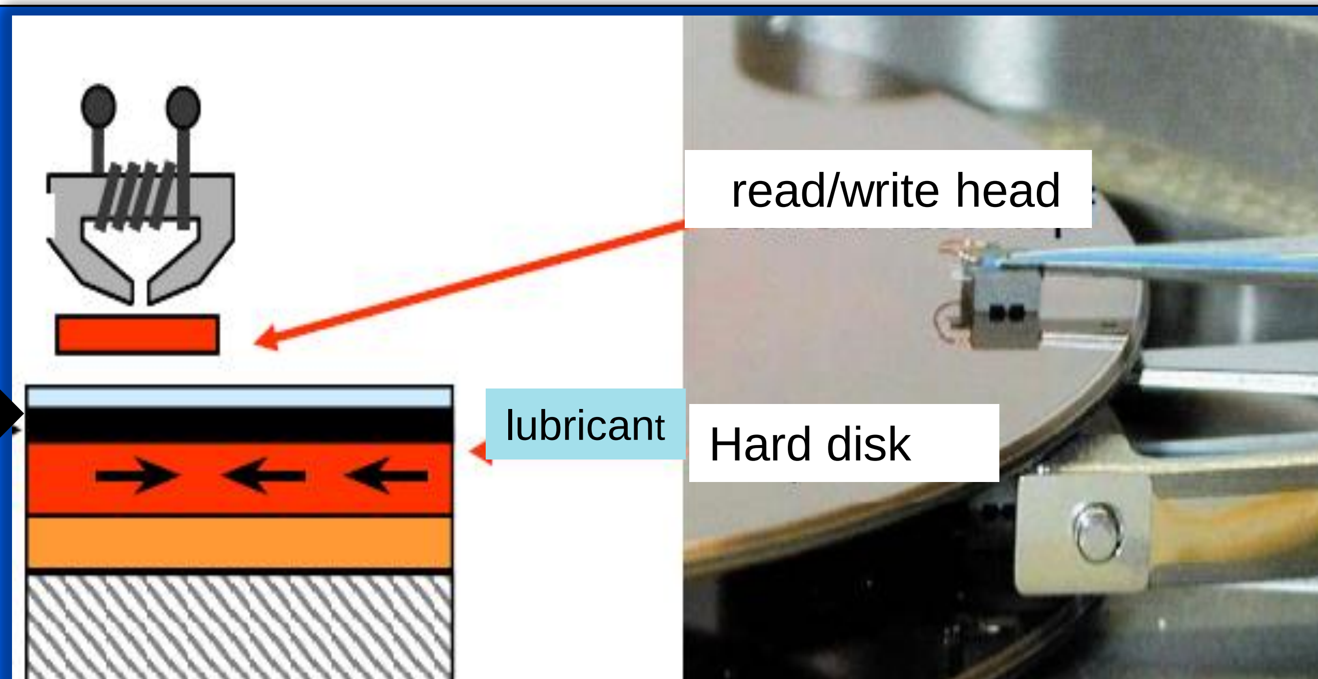
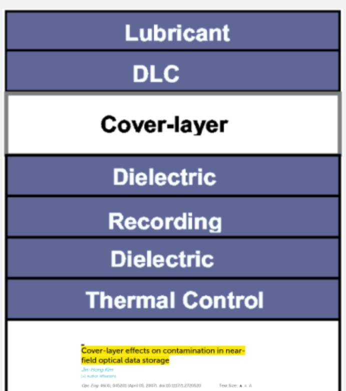
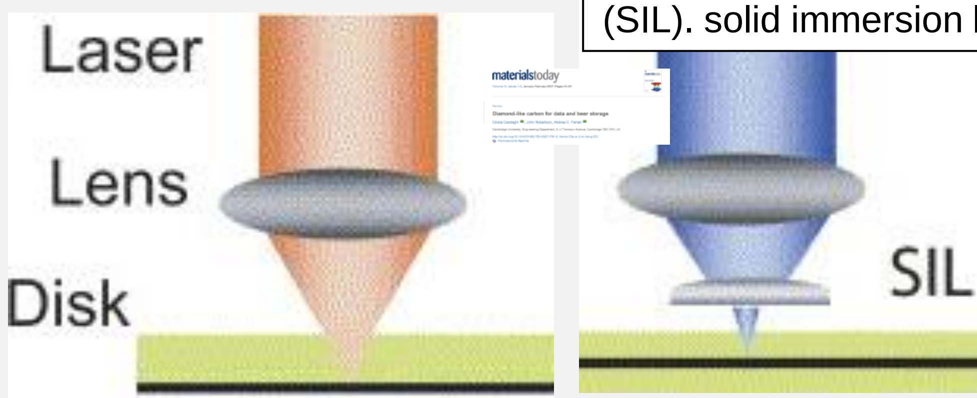


Carbon coating

Magnetic layer
Cr underlayer
Substrate







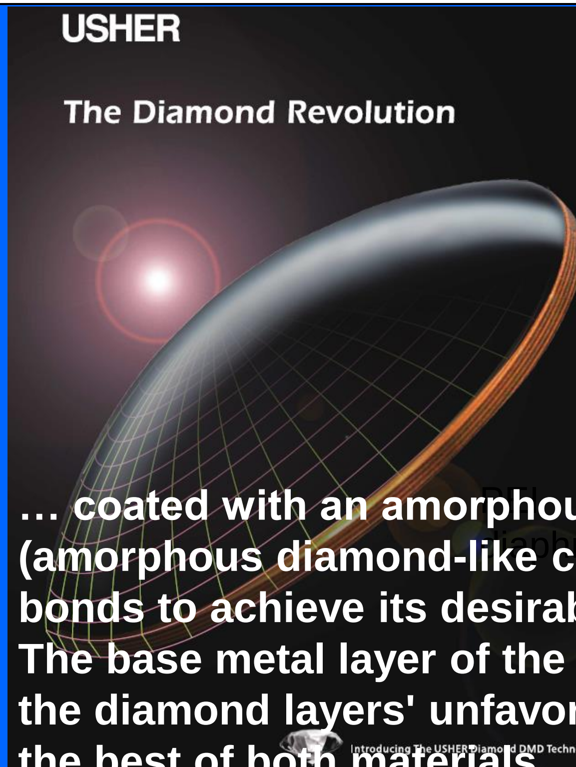
(SIL). solid immersion lens

Applications of DLC 2: scratch resistant coatings: glass

DiamondHard® technology:
coating the lenses with a DLC
- provides scratch-protection
- additionally reduces surface friction:
so that the lenses shed water
more easily to reduce spotting.

The use of infrared optical systems often requires the protection of exposed front surfaces against extreme environmental impacts.

Applications of DLC 3: acustic: loud speakers ….



… coated with an amorphous diamond-like carbon layer .. (amorphous diamond-like carbon has mixed sp3 and sp2 bonds to achieve its desirable properties) on both sides. The base metal layer of the Diamond DMD dome tames all the diamond layers' unfavorable sonic traits and brings out the best of both materials.

Pioneer

7.7 cm cone midrange speaker
with multiple pulp fiber composite diaphragm
Ion-plated DLC (Diamond-like Carbon)-coated titanium center cap

http://www.pioneer.ph/ProductDetail/default.asp?ProductId=544&CatId=89

Applications of DLC 4: gas barrier coating

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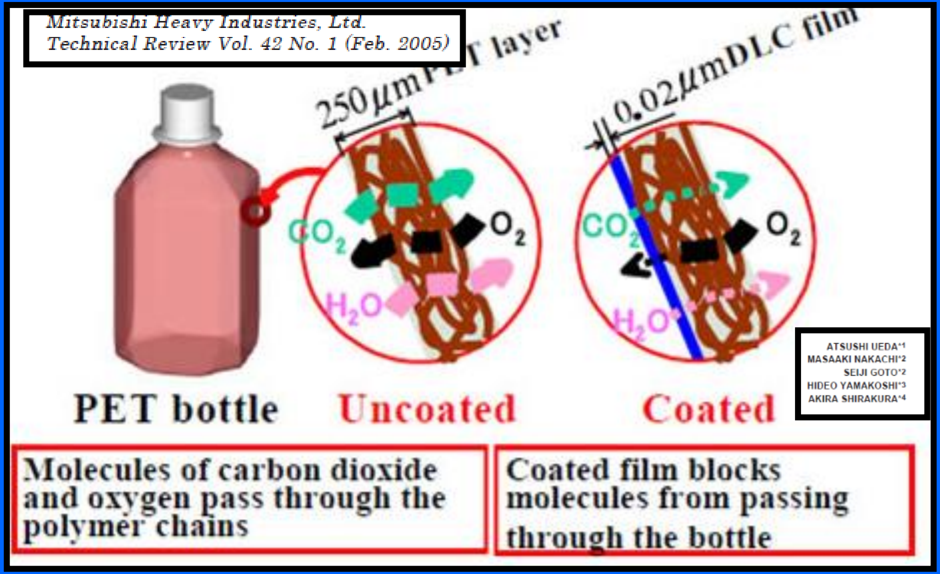

Applications of DLC 5: medical

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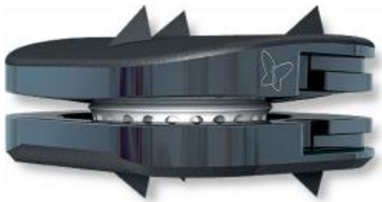
New challenges in medical applications

We are looking for spare parts !

Examples dental applications

cervical spinal disc
(Discmaxx C®, Maxxspine)
DLC coated bearing surface

cervical spinal disc
fixed PE nucleus
DLC coated endplate
(BAGUERA®C, spineart)



DLC coated condylar head
(MODUS Reco 2.5,

Figure 1: Amorphous Silicon Carbide-coated Cobalt–Chromium Coronary Stent

The compacted form of the aSiC:H-coated CoCr stent (PRO-Kinetic Coronary Stent with PROBIO® coating, Biotronik AG, Switzerland), with its characteristic blue-brown colouring, wrapped around a balloon catheter. Source: BIOTRONIK AG, Switzerland.

Hip, knee implants limited/no success only …

a) … c) An overview on diamond-like carbon coatings in medical applications to be published
R. Hauert[1], K. Thorwarth[1], G. Thorwarth[2],

Applications of DLC 6: Razor blades and “Decoration”

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Get a close comfortable shave even on Day 30 with Gillette Mach 3 razor. This is because it has 3 Blades with Diamond like coating that stay sharp longer to give you a great shave even on Day 30

DLC coated stainless steel
schofieldwatchcompany.com

Applications of DLC 7: tools: forming / cutting / plastics

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DLC against: smearing of aluminium on the tool surface

Form-giving mold components (SULZER)

- Less build up of residue on the mold surface
- Better protection against corrosion
- Less abrasive wear
- Better protection against scratches
- Preservation of release properties

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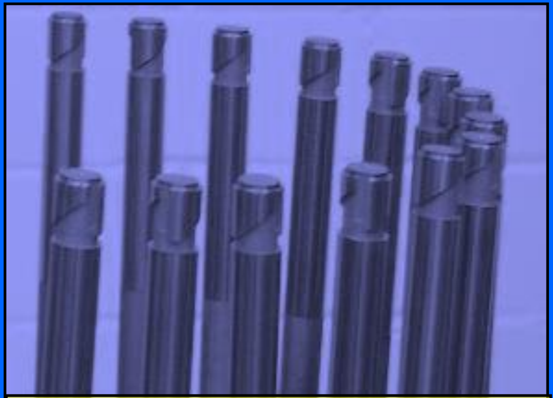
Applications of DLC 8: engineering / components

Machine elements

Parts of pumps



Injection plungers

Ball valves: balls and seat rings

Applications of DLC 9: Gears, transmission ….

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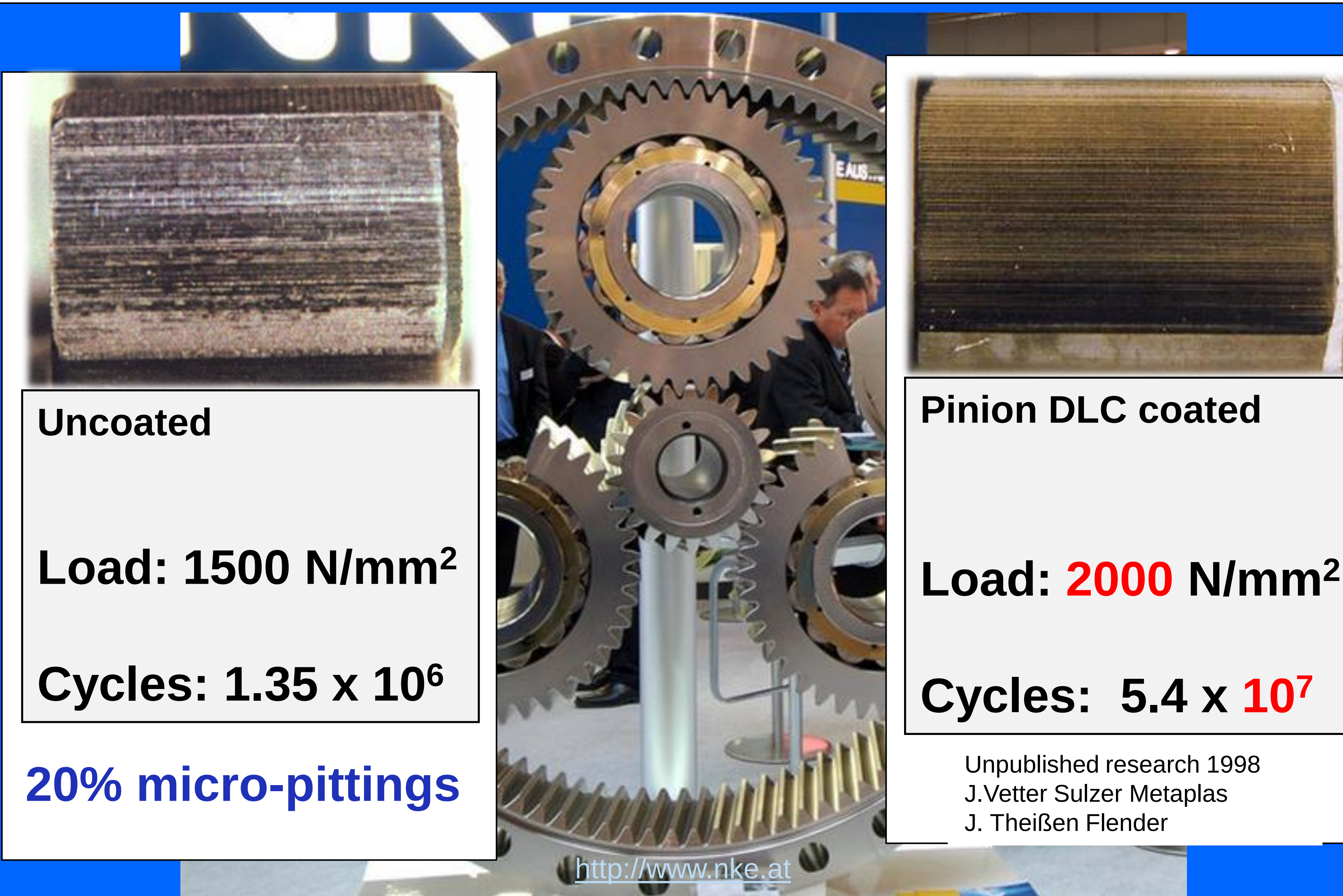

Uncoated

Load: 1500 N/mm^2

Cycles: 1.35 x 10^6

20% micro-pittings

Pinion DLC coated

Load: 2000 N/mm^2

Cycles: 5.4 x 10^7

Unpublished research 1998
J.Vetter Sulzer Metaplas
J. Theißen Flender

http://www.nke.at

Applications of DLC 10-1: automotive

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20 years ago: Success of DLC started with RACING APPLICATIONS

CAVIDUR®

Applications of DLC 10-2: automotive: DRIVEN FORCE FRICTION LOSES

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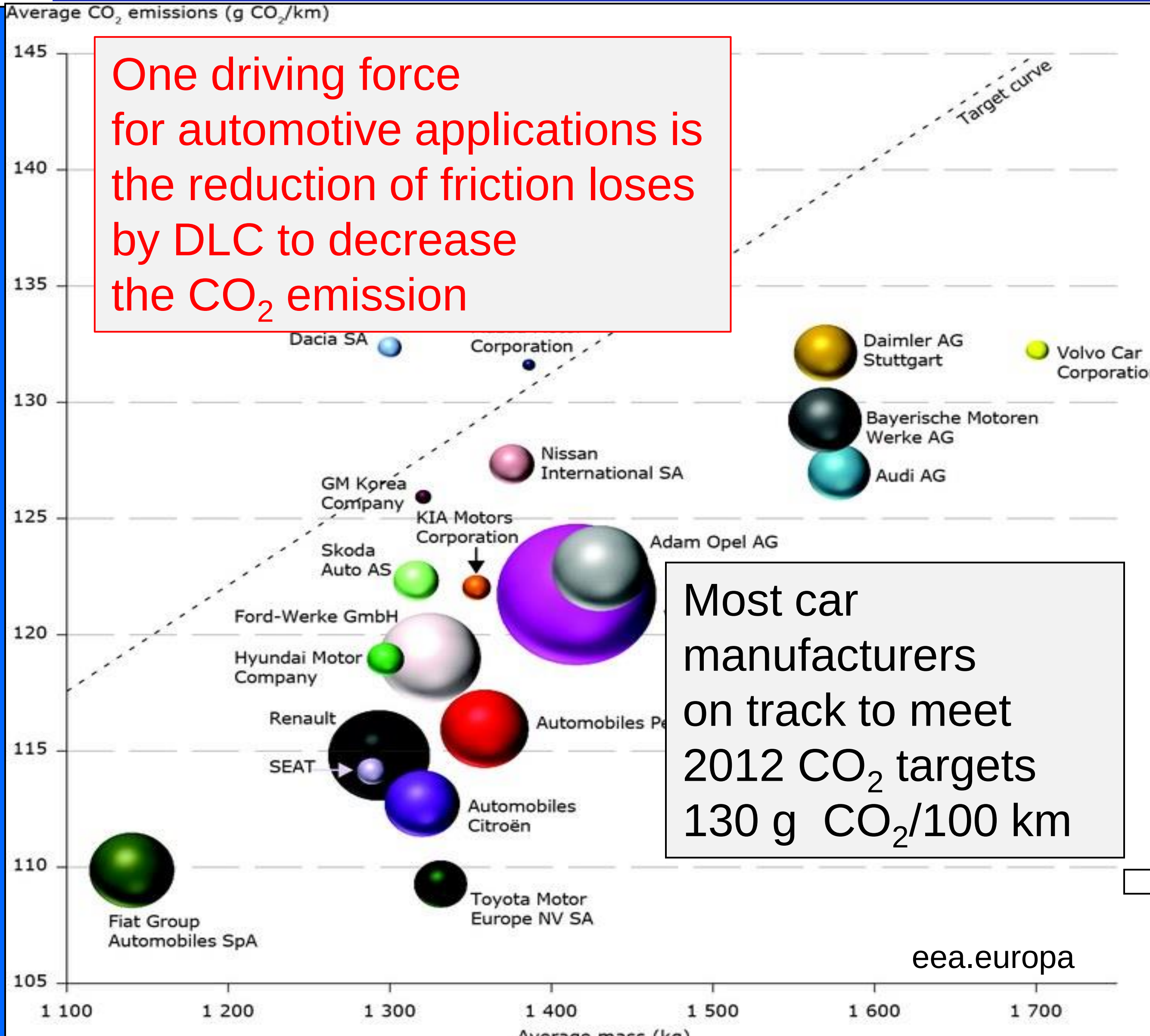

One driving force for automotive applications is the reduction of friction loses by DLC to decrease the CO_2 emission

Most car manufacturers on track to meet 2012 CO_2 targets 130 g CO_2/100 km

And 2020?

The EU has a target for the average new passenger car to emit less than 130 grams of carbon dioxide per kilometre (g CO_2/km) by 2015.
Within this overall target individual manufacturers have specific targets, calculated using the average mass of their fleet. This means that the vehicle fleet can stay diversified by allowing higher emissions from heavier cars than from lighter vehicles. The targets will be gradually phased in to apply to an increasing proportion of cars - 65 % of the fleet I s taken into account for 2012 targets, rising to 100 % in 2015.
Manufacturers have a long-term target

of 95 g CO_2/100km
Petrol: 4,1 l/100 km
Diesel: 3,6 l/100 km

Applications of DLC 10-3: automotive

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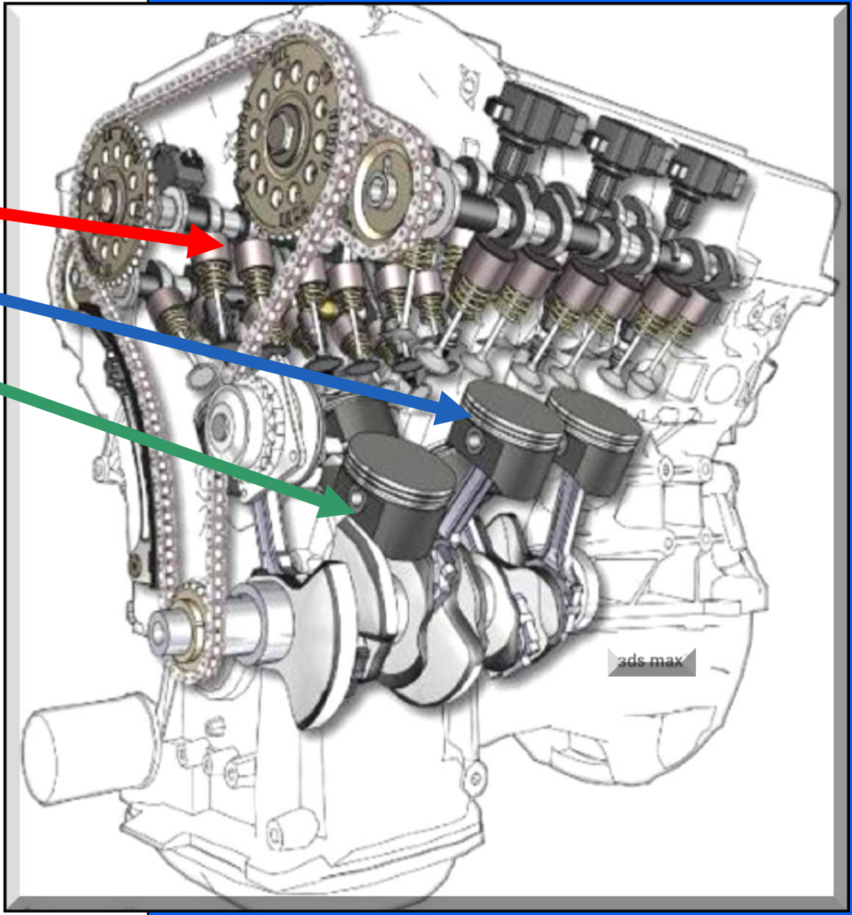
Mass production



Tappets

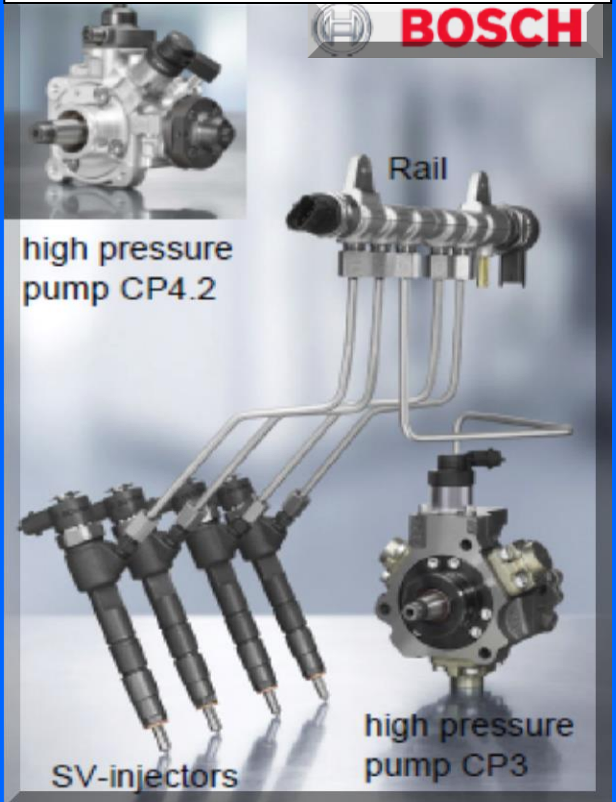
Piston rings

Piston pins

More high end

- Piston skirts
- Camshafts
- Crankshafts
- Fingers
- .....

Injection systems: valve parts/pump



Simplified field C/H/C-Csp3 of a-C:Hx coatings (X = 0 … 40)

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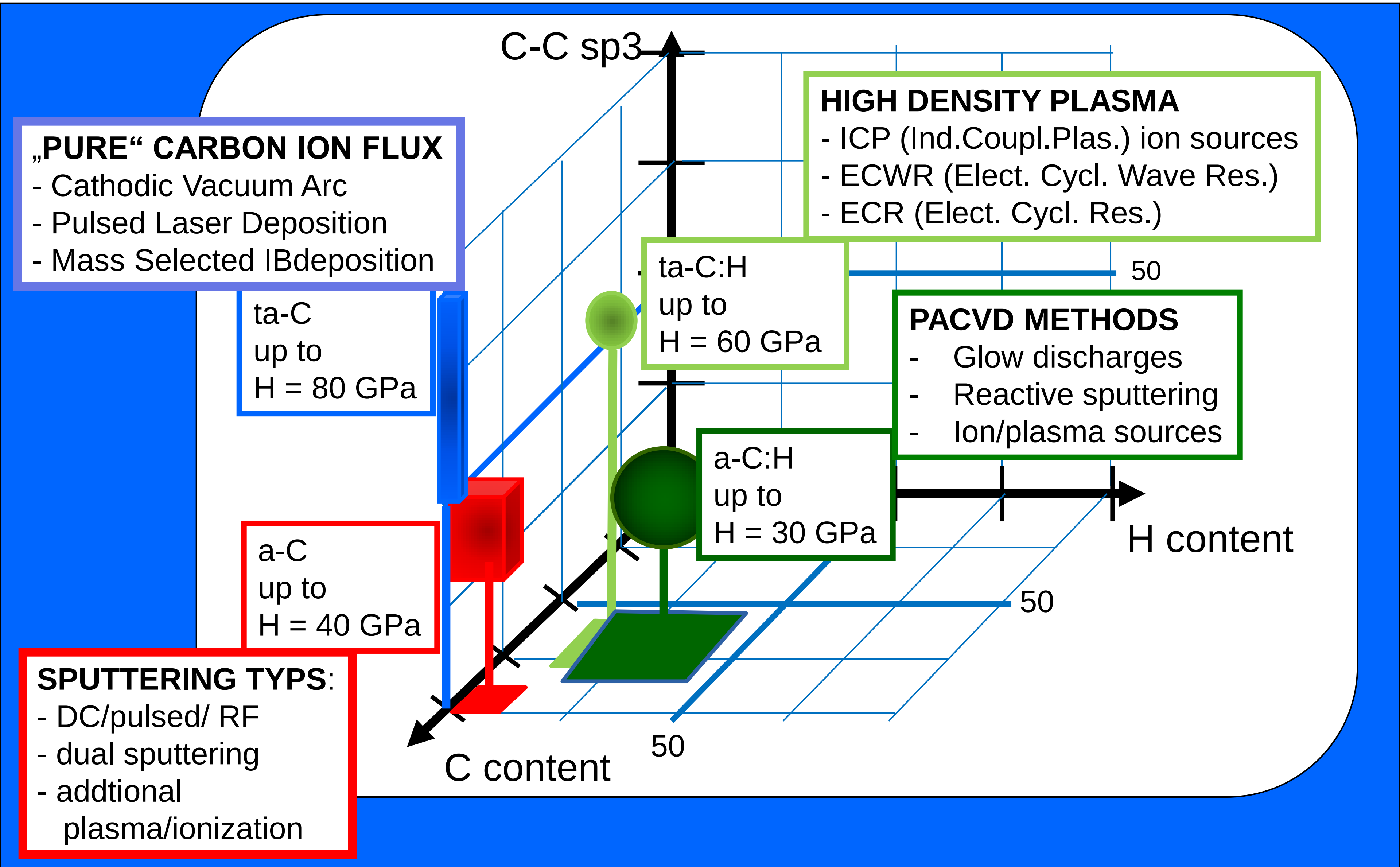

More DLC versions: doping of a-C:H or a-C matrix

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a-C(H)
- high wear resistance
- high hardness

a-C(H)X
- surface energy
- sticking property
- tribo film formation
- electrical resistivity

X: Si, O, F, N, B

HARD CARBON COATINGS

Me: W, Ti, Cr, Zr, Ag

a-C(H)Me
- "ductile"
- electr. resistivity

a-C(H)X:Me
- electrical resistivity
- hardness
- E-modul

The DLC family according the VDI classification

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	Amorphous carbon films **Diamond-like-carbon (DLC)** films							crystalline carbon films diamond films	
additional substance	hydrogen free		metal	containing hydrogen		metal	non-metal		
kind of bonds	sp^2	sp^3	sp^2	sp^2 / sp^3	sp^3	sp^2		sp^3	
shortcut	**a-C**	**ta-C**	**a-C:Me**	**a-C:H**	**ta-C:H**	**a-C:H:Me** (Me = W, Ti, ...)	**a-C:H:X** (X = Si, O, N, F, B)	**-**	**-**
usual names	**DLC, graphitic carbon**	**DLC i-C diamond**		**DLC, hard carbon**		**DLC Me-DLC Me-C:H MeC:H**	**DLC X-DLC Si-DLC**	PCD, PD, CVD-diamond	
deposition processes	**PVD**	**PVD**	PVD	**PA-CVD**	PVD PA-CVD	**PVD PA-CVD**	**PVD PA-CVD**	aktivated CVD	

DLC coatings : properties cover a wide field more than steel grades, but its always amorphous !

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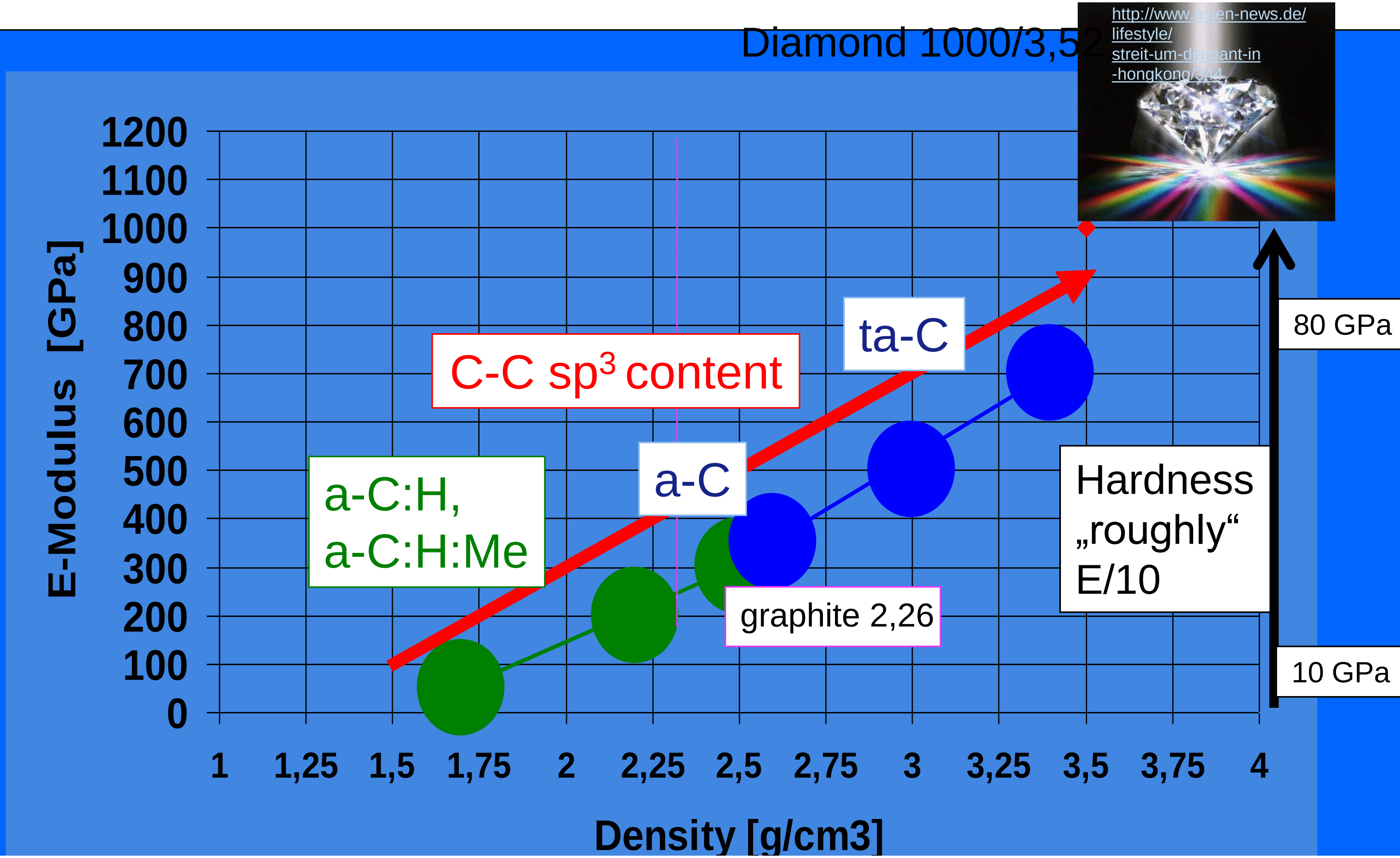

Coating thickness start at 2 nm up to 10.000 nm (mostly 500 nm to 4 000 nm)

Most important industrial deposition methods for DLC coatings on 3D parts

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- „Pure DLC“ Amorphous Carbon Coatings
  - PVD
    - cathodic arc
    - sputtering
  - PACVD
    - Plasma/ion sources
    - Glow discharges
- Coating systems with underlayers
  - Hybrid processes PVD + PACVD
    - Sputtering + DLC
    - Arc + DLC
    - e-beam + DLC

Not shown here:
PLD: Pulsed Laser Deposition and
PBIID: Plasma Based Ion Implantation and Deposition
REASON: Limitations in industrial application

Most important industrial deposition methods for DLC coatings on 3D parts

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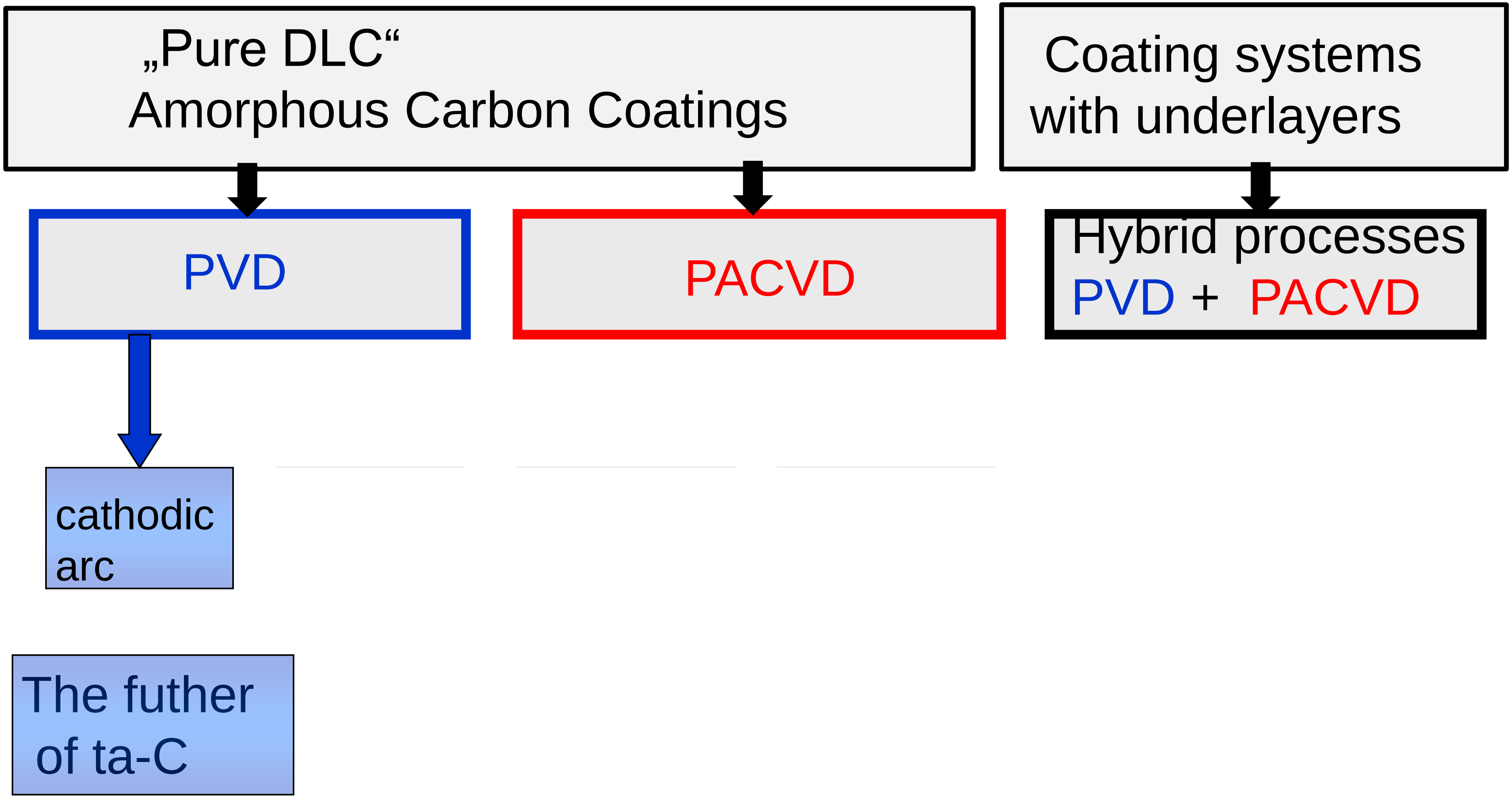

ta-C: PIONEERING WORK:
- deposition methods SOVIET UNION: Kharkov Institute off Physics and Technology
- automotive application in large scale: NISSAN

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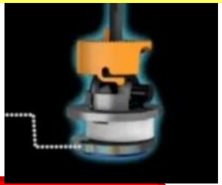
Delta::
sealing of cocks

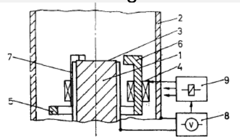
Nissan: valve lifter

DELTA Water Faucets



DC "DIRECT" ARC
Romanov/A.A. Andreev
Sovite Uniion confidentiality
others till 1979
V. E. Strelnitskij, N. N. Matyushenko, V. T. Tolok; I. I. Aksenov, S. I. Vakula, V. G. Padalka

DC ARC ta-C Germany
B.Rother
J.Vetter
J. Siegel



Development &
selected small scale application::
tools, compoments, medical applications
hard discs,

mass production

development of deposition methods

1975 — 1985 — 1995 — 2005 — 2015

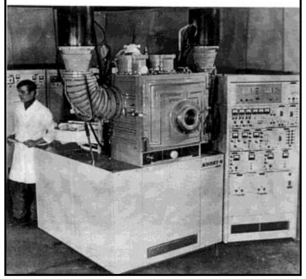
1976

FIRST PAPER: ta-C:
Thermal stability
N. N. Matyushenko,
V. E. Strel'niskij,
A. A. Romanov

1978

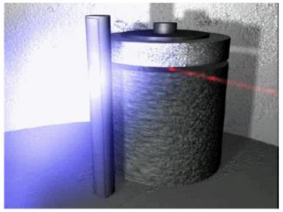
FILTERED DC ARC t-aC
Aksenov, I.I.,
Belous, V.A.,
Padalka, V.G.,
Khoroshikh, V.M.

Setup with toroidal (90°) plasma filters



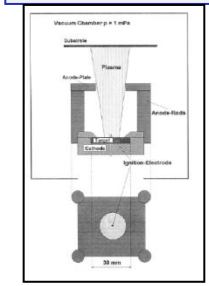
1991

LASER ARC
H.J.Scheibe, P.Siemroth,
W.Pompe, B.Schöneich



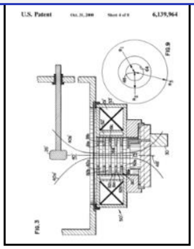
1994

HIGH CURRENT ARC
P. Siemroth,
T. Schülke,
T. Witke



1995

ENHANCED ARC
P.E. Sathrum, B.F. Coll
US 6139 964



2002

Modulated pulsed
Current
W. Grimm

Different modification of filters,
pulsing
sources
process development

Deposition methodes for ta-C based on vacuum arc for wear, friction, (corrosion) reduction

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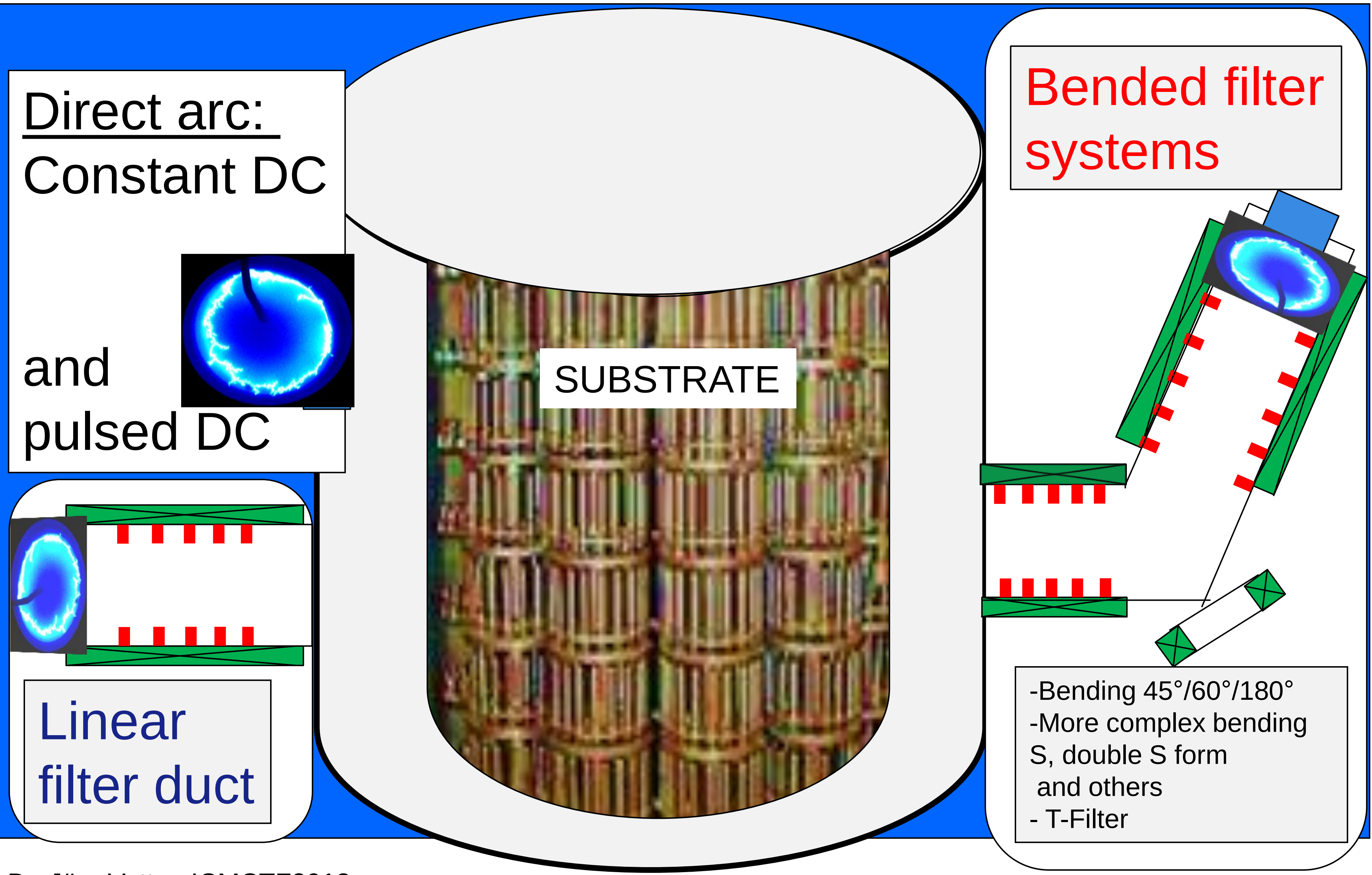
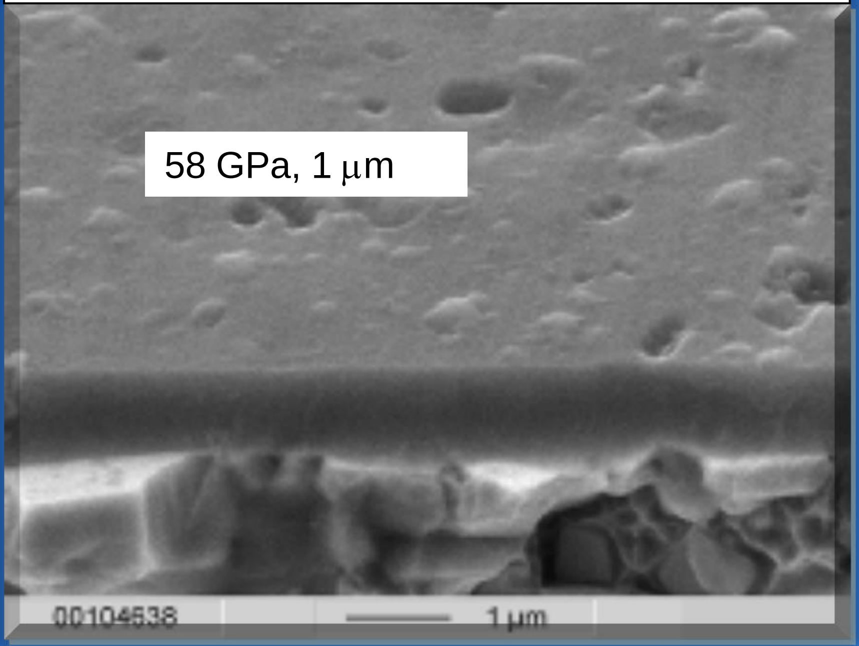


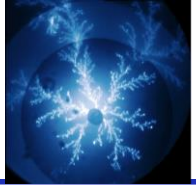
Direct depostion method: constant current mode

APA
Advanced
Plasma
Assisted
evaporators

Optimized:
- graphite cathodes for arc
- magnetic field
- process



Direct deposition method: pulsed arc modes



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Mechanical triggering

W. Grimm
Pulse length 0, 3 ms
Base current 50-100 A
Pulse current 1500 A
Frequency 100 Hz

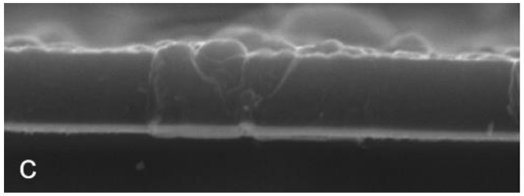
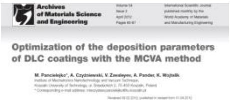


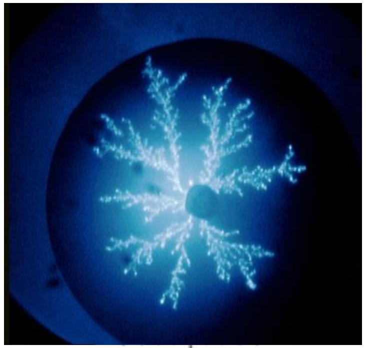
Fig. 1. SEM fracture images of DLC coatings with a Cr sublayer: a) DLC - 0.9 µm, Cr - 0.03 µm; b) DLC - 1.4 µm, Cr - 0.1 µm; c) DLC - 1.8 um, Cr - 0.3 um

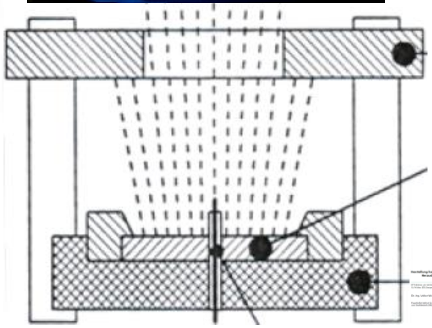

Archives of Materials Science and Engineering

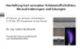
Optimization of the deposition parameters of DLC coatings with the MCVA method

Electrical triggering by central electrode

Fhg IWS/Arc Precision: **HCA**
P. Siemroth
Pulse length ca. 1ms
Current kA range
Frequency ca. 300Hz



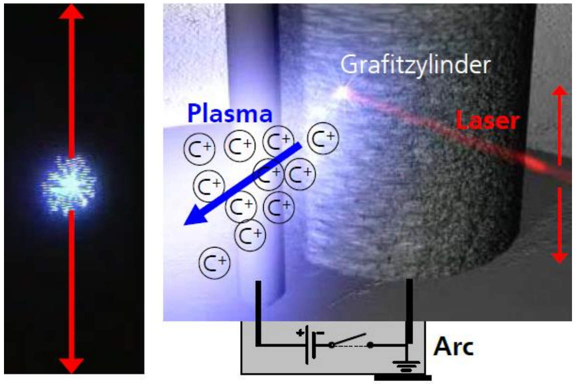




Central triggering electrode

Laser triggering by external laser

Fhg IWS:
Scheibe/Siemroth
Pulse length ca. 0,1 ms
Current kA range
Frequency ca. 300 Hz



Bended filter: pulsed arc process: ta-C by arc for heads

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TFMH coating film technology
thin diamond-like carbon (DLC) films for longer lasting TFMH slider overcoats and landing pads.
Pulsed Filtered Cathode Arc Source
to enable sub 2 nm overcoat thickness.

Filtered Arc 1978:
Aksenov, I.I., et.al.

1976: ta-C:
First paper
N. N. Matyushenko,
V. E. Strel'niskij,
A. A. Romanov

Thin-film magnetic head (TFMH)

ta-C: Different industrial filter set ups: tool and component coatings

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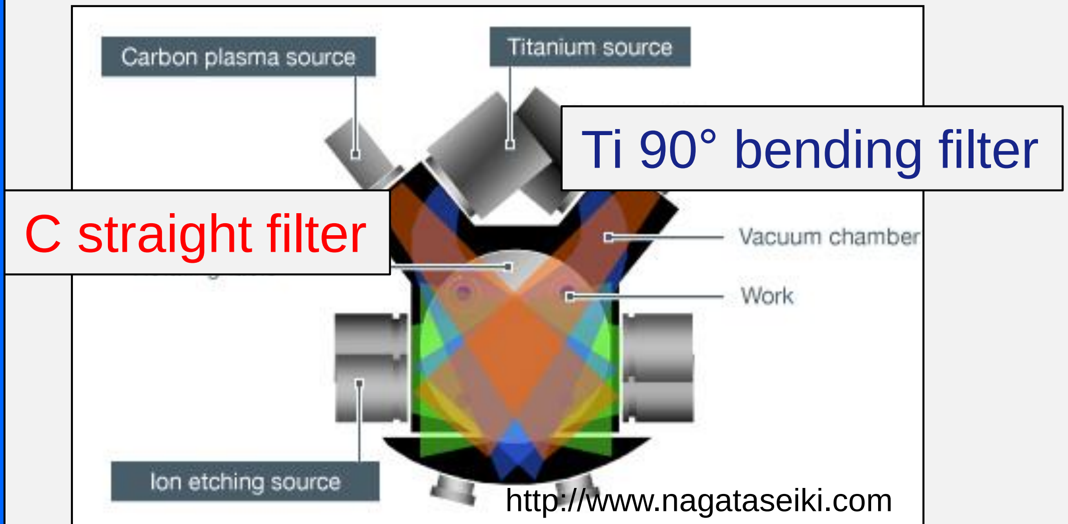
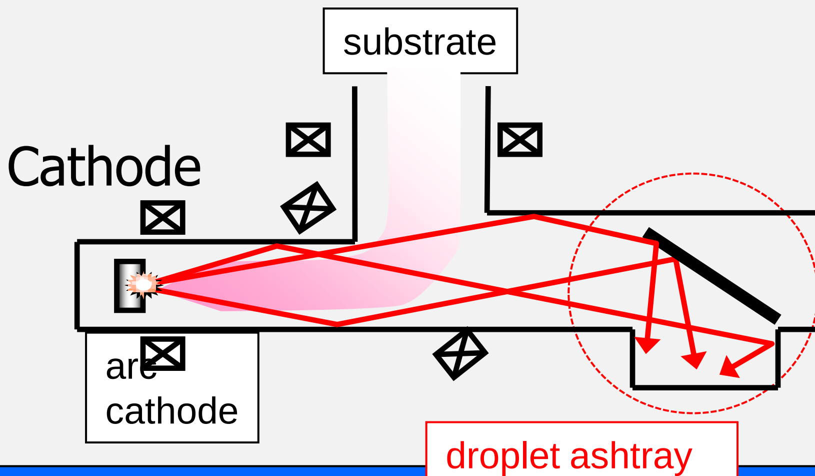
Linear filter for carbon, bended filter system metal (Ti) tools components



T- filter for ta-C coatings: droplet ashtray



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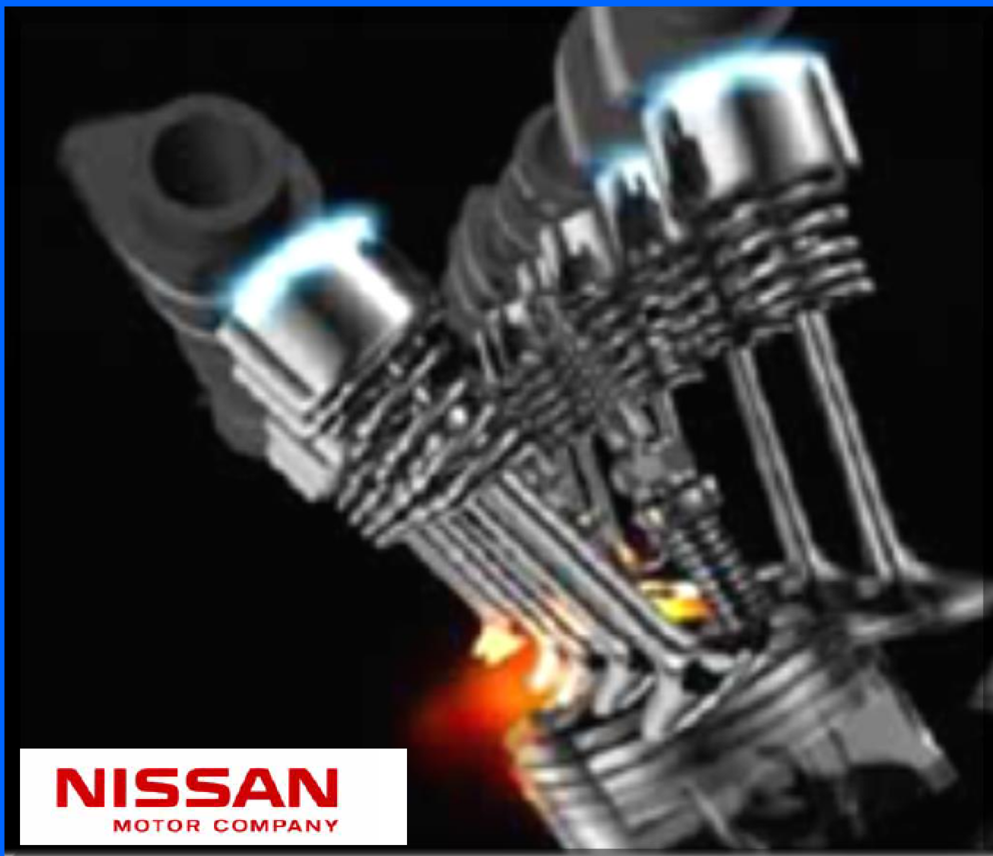
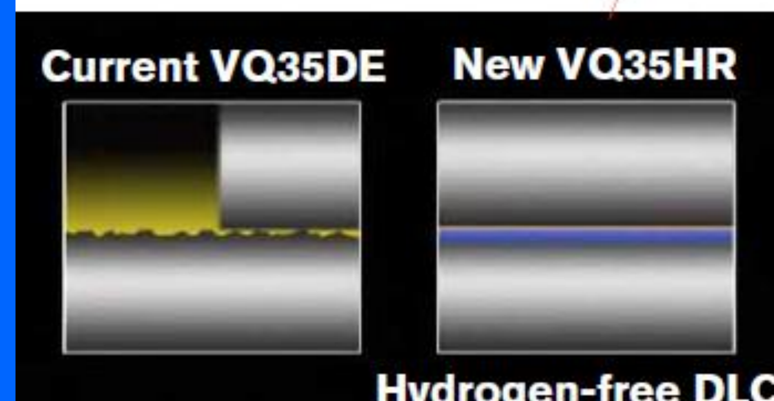
Cam-valve lifter friction reduction by 40%



Optimized lubricant

Thickn. ca. 500 nm
Hardn. ca.50 GPa
works excellent



Most important industrial deposition methods for DLC coatings on 3D parts

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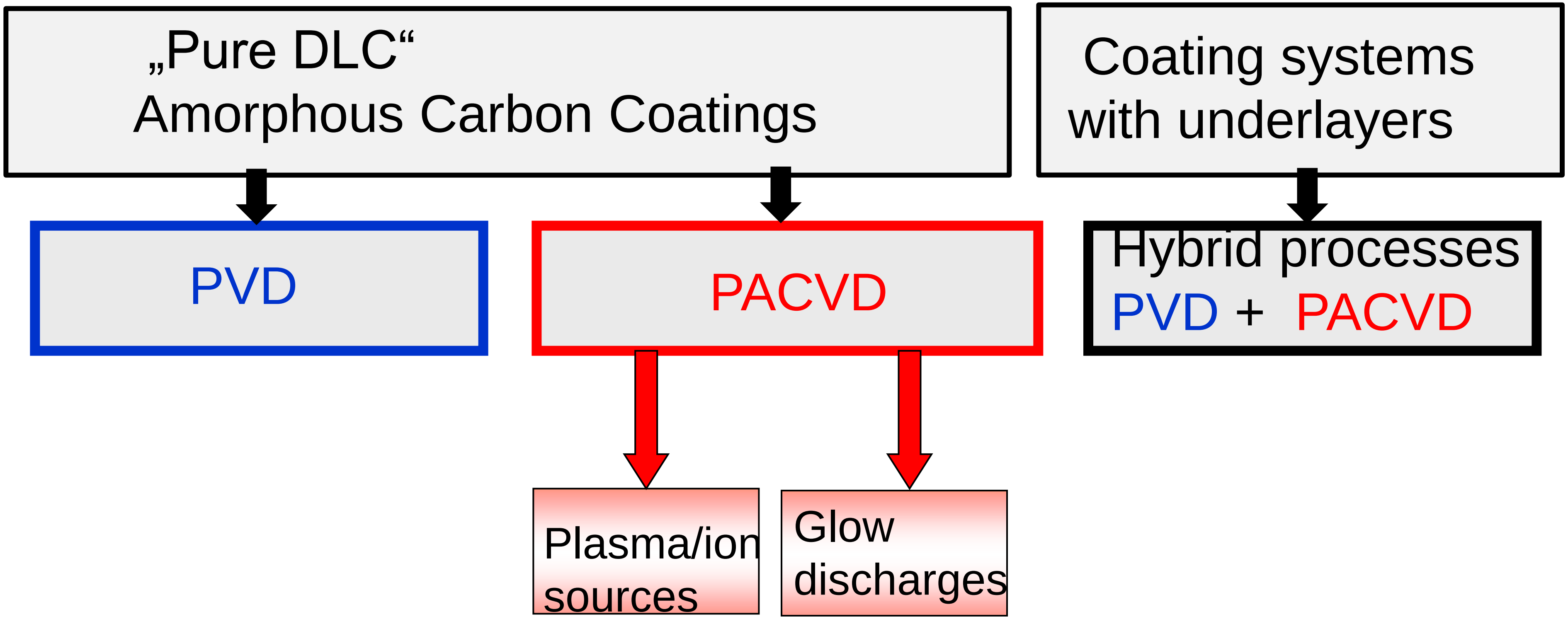

a-C:H:X: History – Highlights

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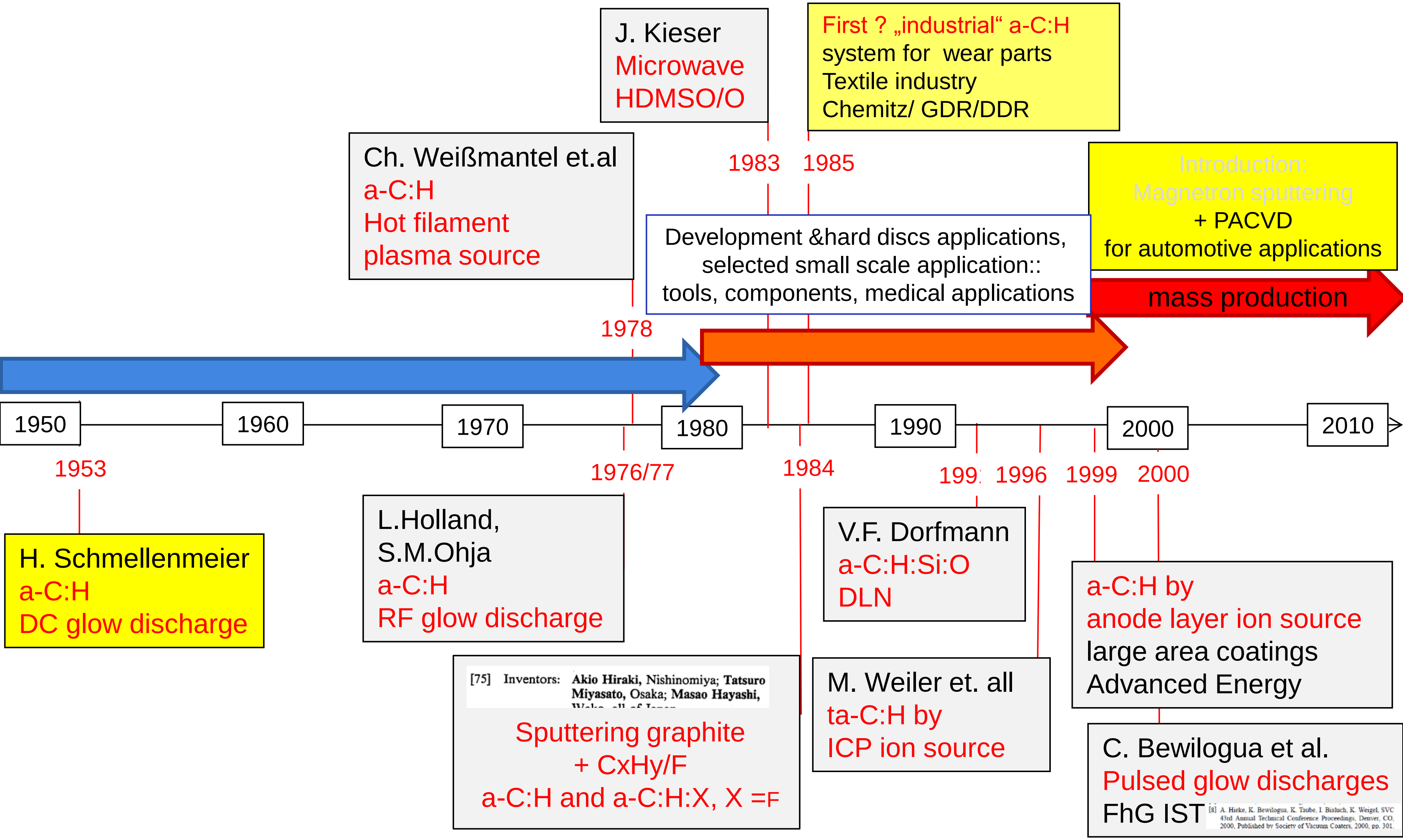

Dr. Jörg Vetter, ICMCTF2013

Most important industrial deposition methods for DLC coatings on 3D parts

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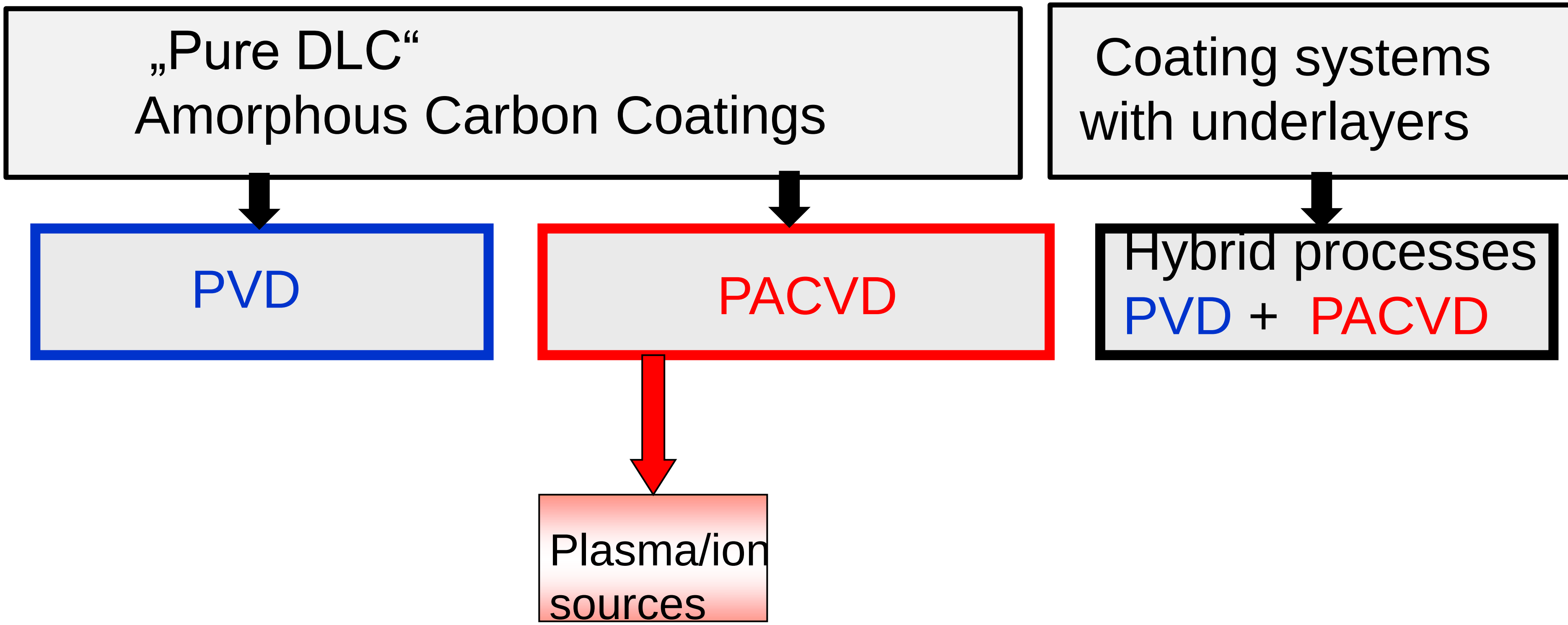

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Sulzer Metco

DLC by Plasma/Ionsources

"Ion sources"

Hall sources

RF-sources ICP

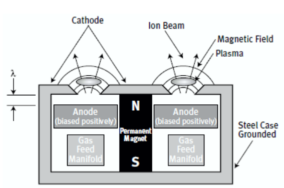
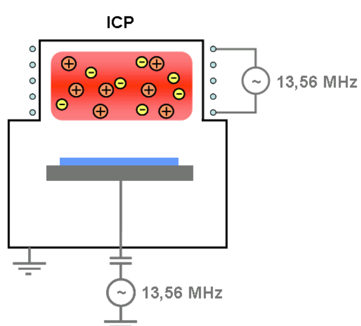


Figure 2. Linear ion source physics

ADVANCED ENERGY

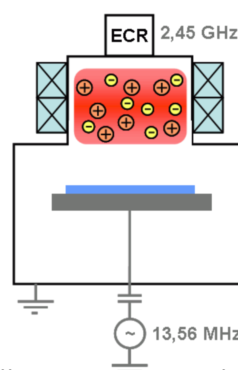


https://www.crystec.com/triplad.htm

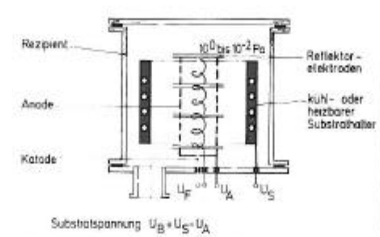
"Plasma sources"

Microwave

Hot filament discharge



https://www.crystec.com/triplad.htm



C. Weissmantel development

DLC by Plasma/Ionsources

"Ion sources"

- Hall sources
- RF-sources ICP

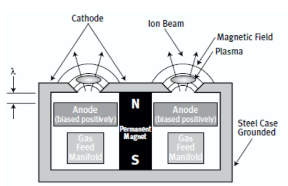
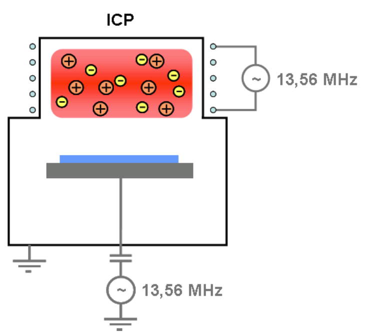


Figure 2. Linear ion source physics

ADVANCED ENERGY®



https://www.crystec.com/triplad.htm

Selected ion sources used for DLC coating processes

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Sulzer Metco

Anode layer: hall curent source

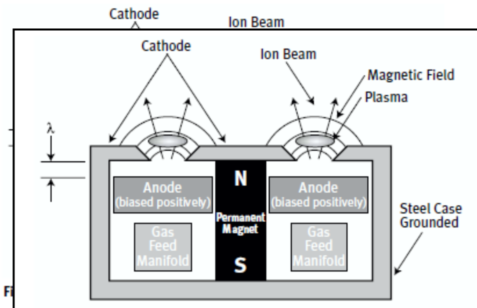


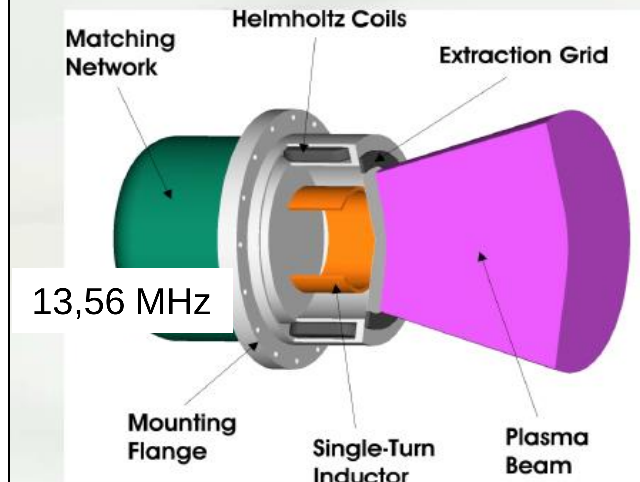
Figure 2. Linear ion source physics

Figure 1. Linear ion source

ICP ion source

Also used for ta-C:H

Schematic of the COPRA Source



Linear COPRA – Source for dynamic deposition!

CCR TECHNOLOGY

Anode Layer Hall Sources: Flat Glass Coater

SULZER
Sulzer Metco

Diamond-Like Carbon as a protective coating for decorative glass

Glass Performance days 2009

Rolf Petrmichl[1], RPetrmichl@guardian.com; Victor Veerasamy[1], VVeerasamy@guardian.com;
Nestor Murphy[1], NMurphy@guardian.com; Jiangping Wang[1], JWang@guardian.com;
Fabio Reis[2], FReis@guardian.com; Maximo Frati[1], MFrati@guardian.com; Jens Peter Mueller[3], JMueller@guardian.com
[1] Guardian Industries USA
[2] Guardian Industries Brasil
[3] Guardian Industries Luxembourg

Figure 13
Decorative glass applications

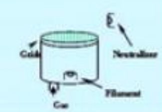
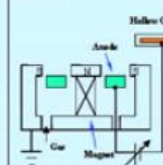
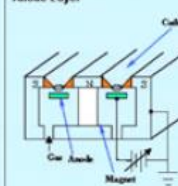
Type	Kaufman Gridded 	Closed Drift 	Anode Layer 
Electron Source	Thermionic or RF-plasma	Thermionic	Cold cathode
Ion Extraction	Multiple grids	Hall effect	Hall effect
Ion Energy (eV)	50 – 1200 (narrow spread)	25 – 120 (broad)	100 – 2000 (broad)
DLC Hardness (GPa)	Up to 40	Up to 30	Up to 60
Maintenance	-	0	0
Gas utilization	0	--	+
Scalability	-	--	+

Figure 3
Types of ion sources

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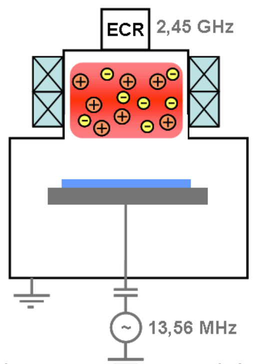
Sulzer Metco

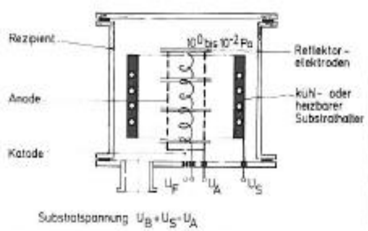
DLC by Plasma/Ionsources

"Plasma sources"

- Microwave
- Hot filament discharge



https://www.crystec.com/triplad.htm

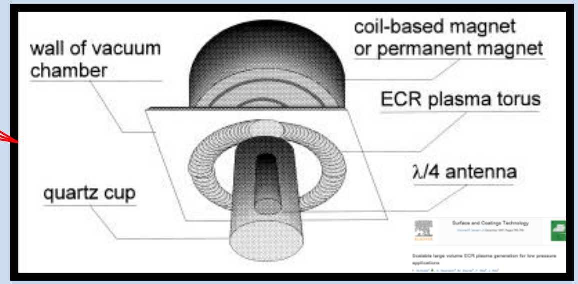


C. Weissmantel development

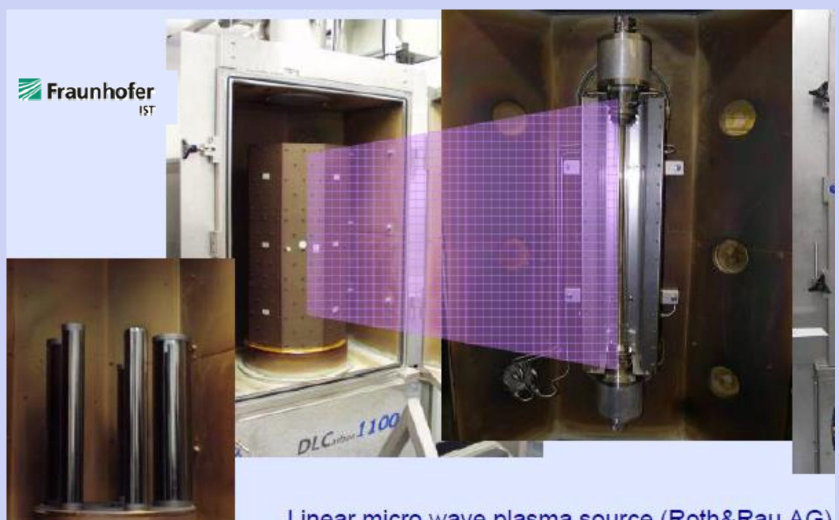
DLC by microwave plasma source

SULZER
Sulzer Metco

Round ECR sources



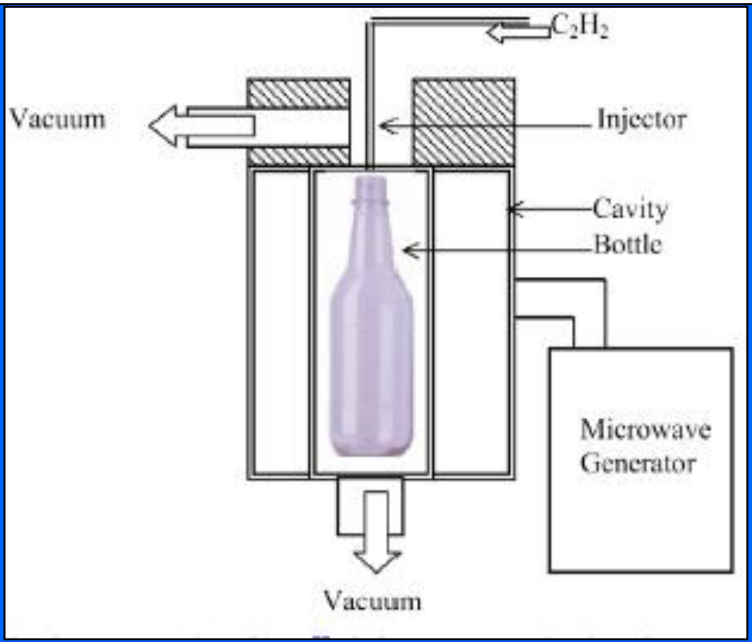
Linear ECR source



Seldom in industrial use

DLC by microwave plasma source: bottles

Sulzer Metco

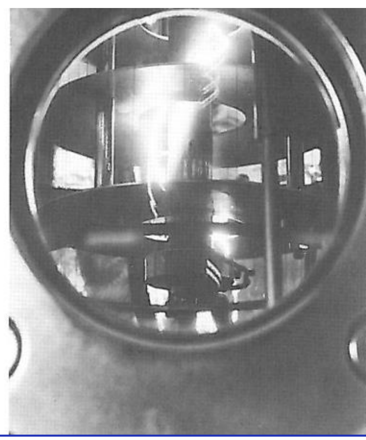


DLC: Hot filament discharge as a plasma source

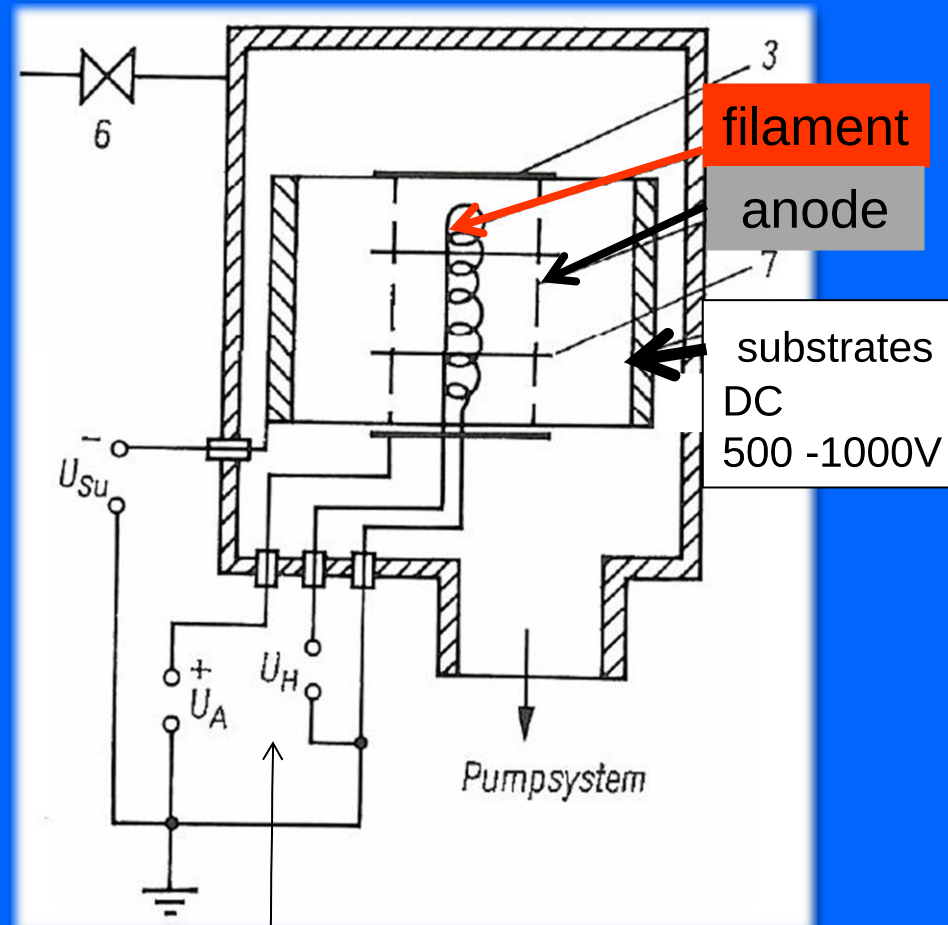
SULZER
Sulzer Metco

Prof. Dr. Ch. Weißmantel
TH Karl-Marx-Stadt GDR/DDR
TU Chemnitz

application: textile machines
– thread guides



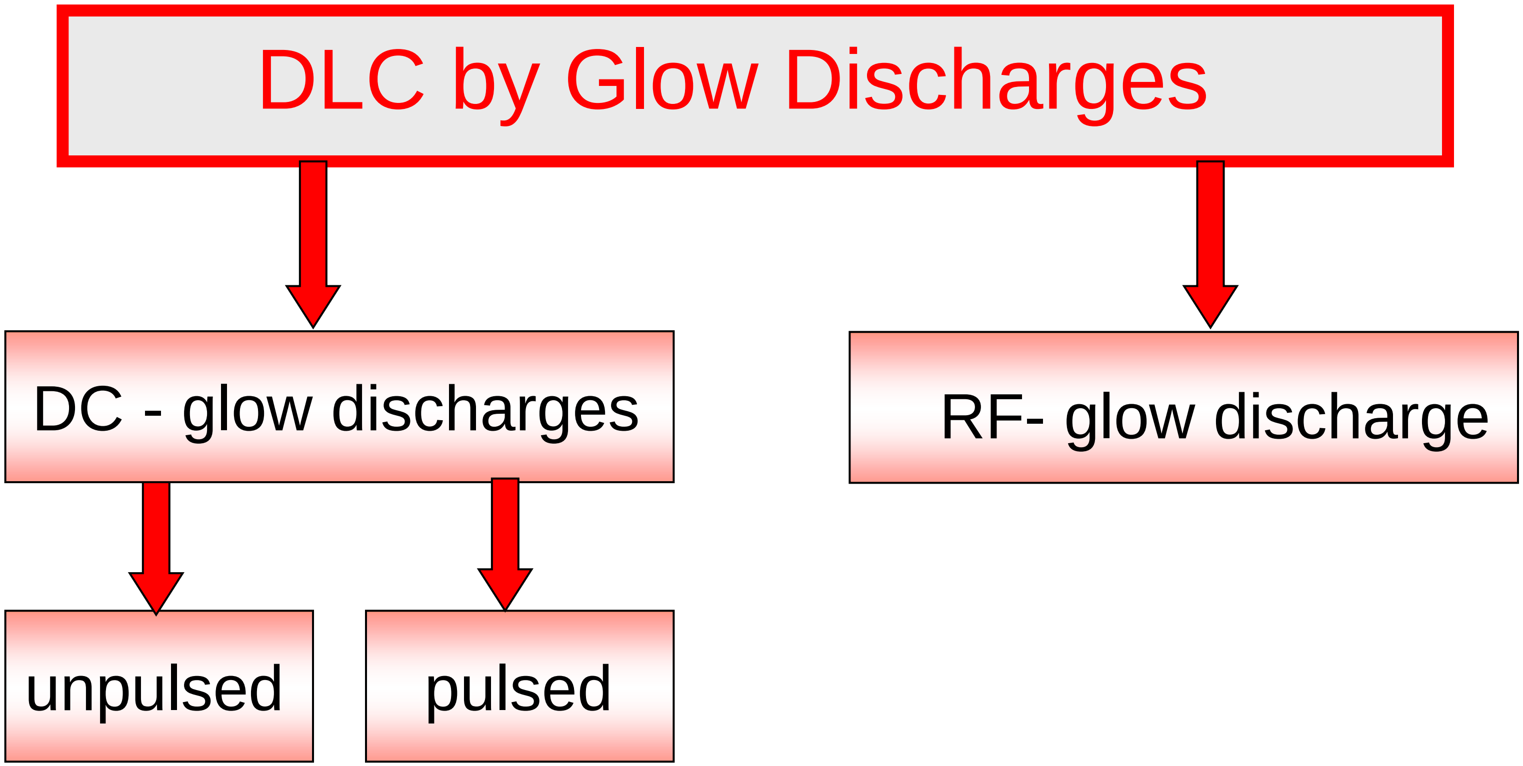
PACVD for a-C:H ca. 1985
in industry Chemnitz (Karl-Marx-Stadt)
development: team Ch. Weißmantel
principe patended 1978



U_H accelaration voltage of injected electrons between the anode and filament: 100 – 250 V

Glow discharge: the muther of DLC

Sulzer Metco



Glow discharge: the muther of DLC

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Sulzer Metco

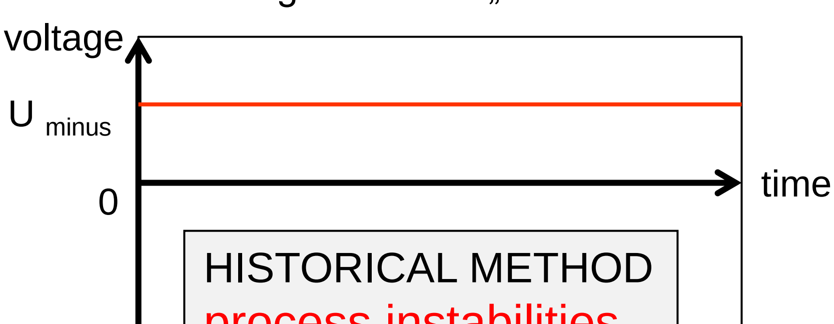
DLC by Glow Discharges

DC - glow discharges

unpulsed

pulsed

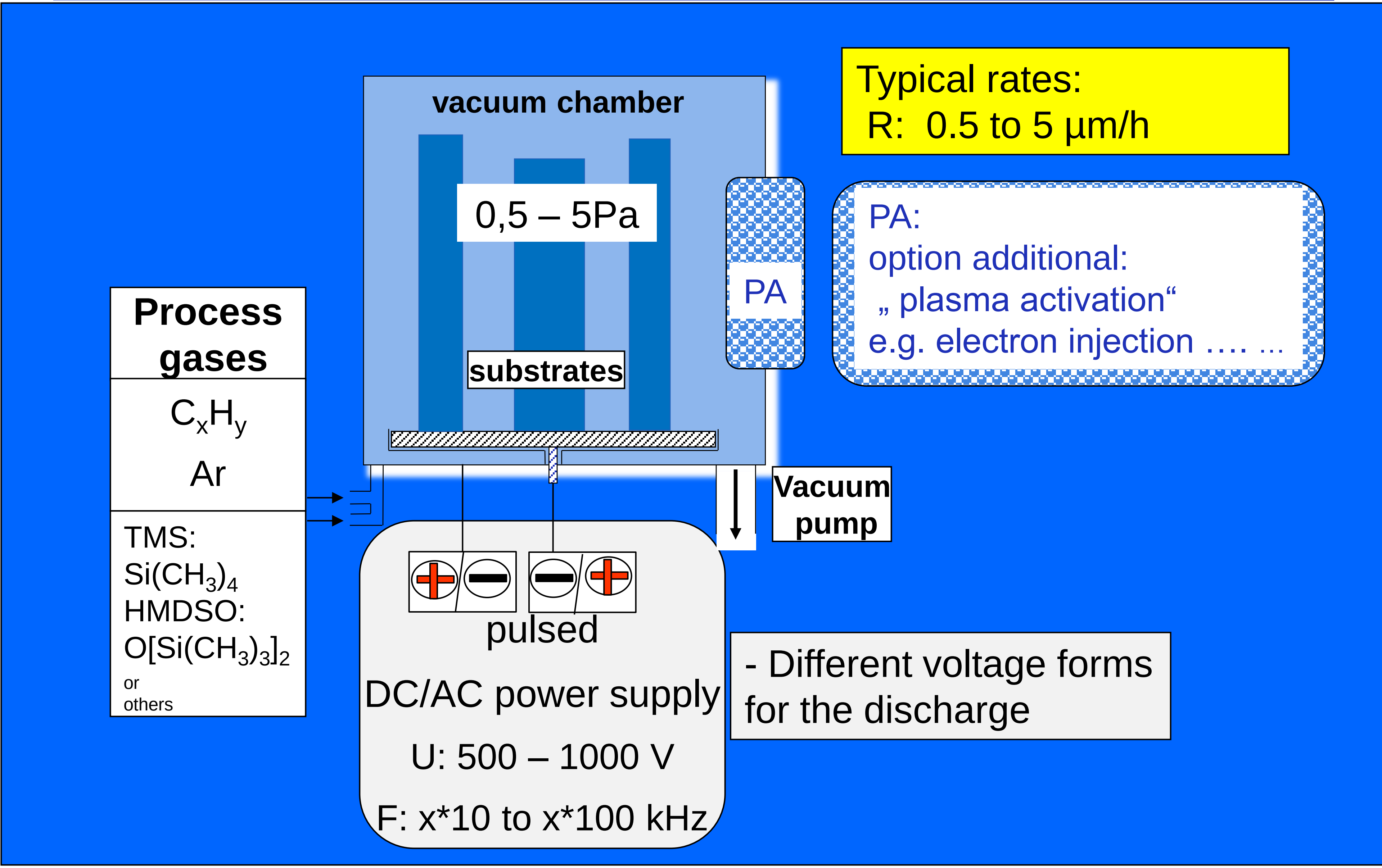
DC voltage form for „direct currents“



HISTORICAL METHOD
process instabilities
caused
by insulation effects

PACVD for DLC by DC/AC glow discharge: typical set up

Sulzer Metco



Voltage forms [non RF (sinus wave)] used for glow discharges (biasing) in DLC processes

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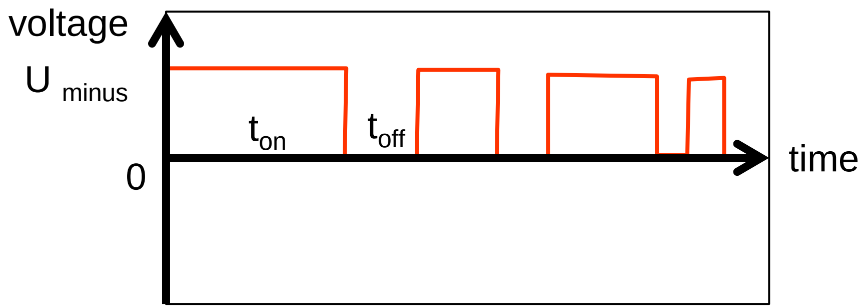
Sulzer Metco

Pulsed DC voltage for "direct currents"



Pulsed DC „rectangular" or „sinusoidal-like"

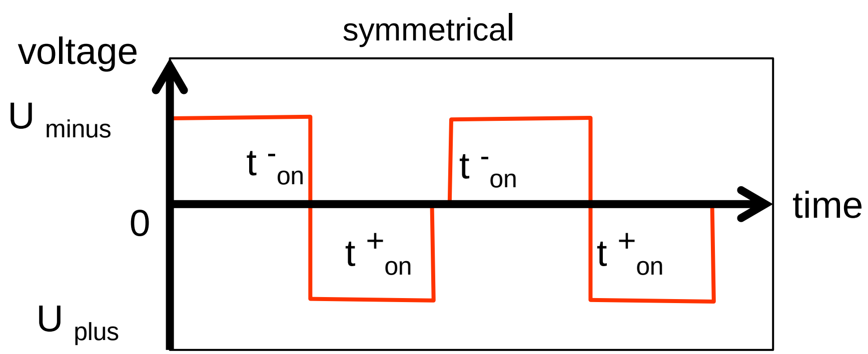
Very Low Frequency VLF: 3-30 kHz,

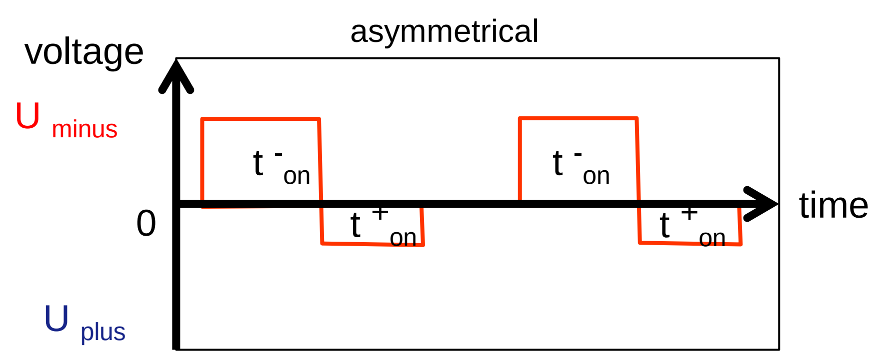
Low Frequency LF: 30-300 kHz

Medium Frequency MF: up to 350 kHz

Pulsed AC voltage for „alternating currents"

U_{minus} ions impinge the substrate:
voltage/current determine the coating properties





Probably most used in application

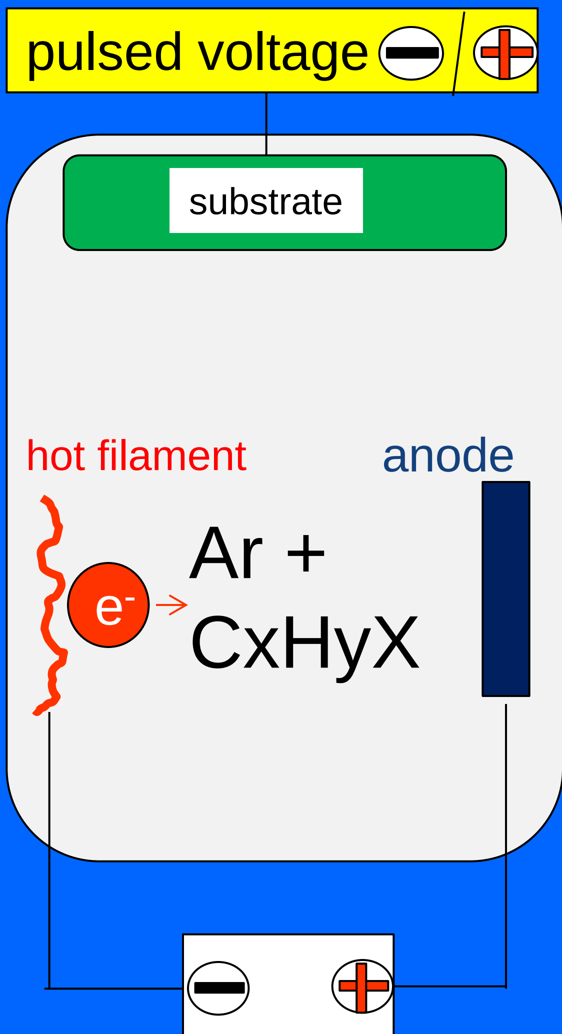
U_{plus} electrons flow from the substrate: decharging effect

SULZER: PACVD for a-C:H:X by glow discharge: pulsed plus „plasma source"

Sulzer Metco

DYLYN®

Diamond like nano composite (DLN): a-C:H/Si-O network

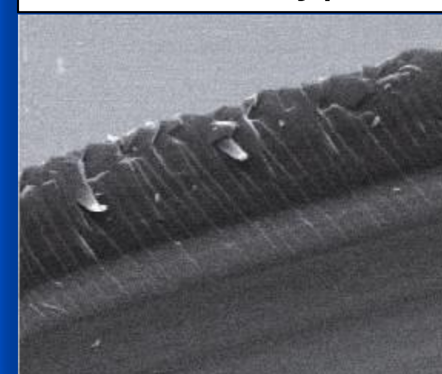


Large chamber for mass production

Different precursor are used for DLN

Precursor	Formula	Mol. weight, g/mole	Boiling point, °C	Physical state
HMDSO	$C_6H_{18}OSi_2$	162.38	101	Liquid
HMDS	$C_6H_{18}Si_2$	146.38	112	Liquid
TEOS	$SiC_8H_{20}O_4$	208.33	168	Liquid
Silane	SiH_4	32	−111	Gas
TMS	$(CH_3)_3SiH$	74.2	6.7	Liquified gas

a-C:H:X- types



DLC by Glow Discharges

RF- glow discharge

PACVD for DLC by RF- Glow Discharges

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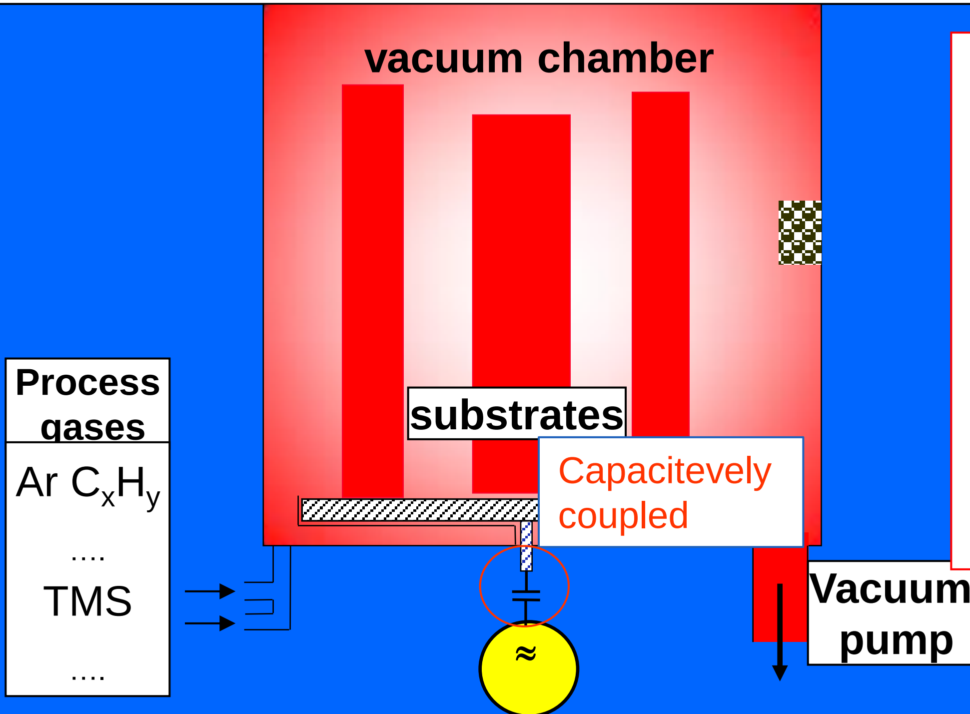
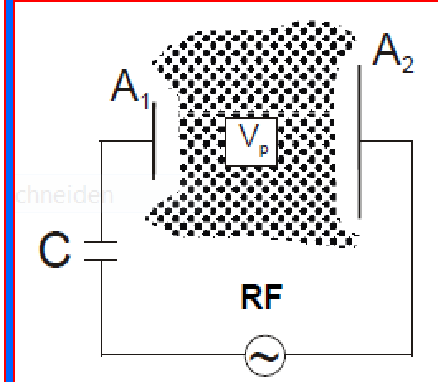
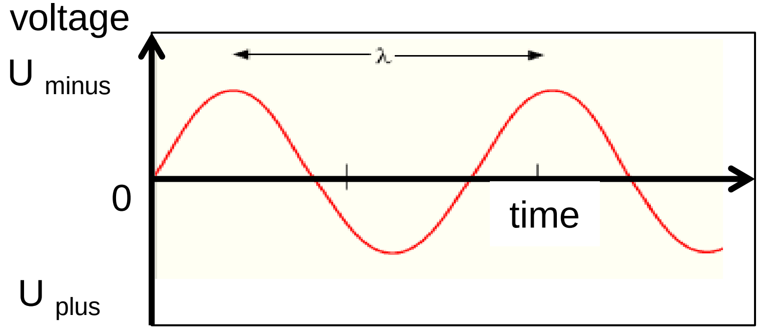


Limitations:
effect of
the substrate
load
on effective
negative voltage

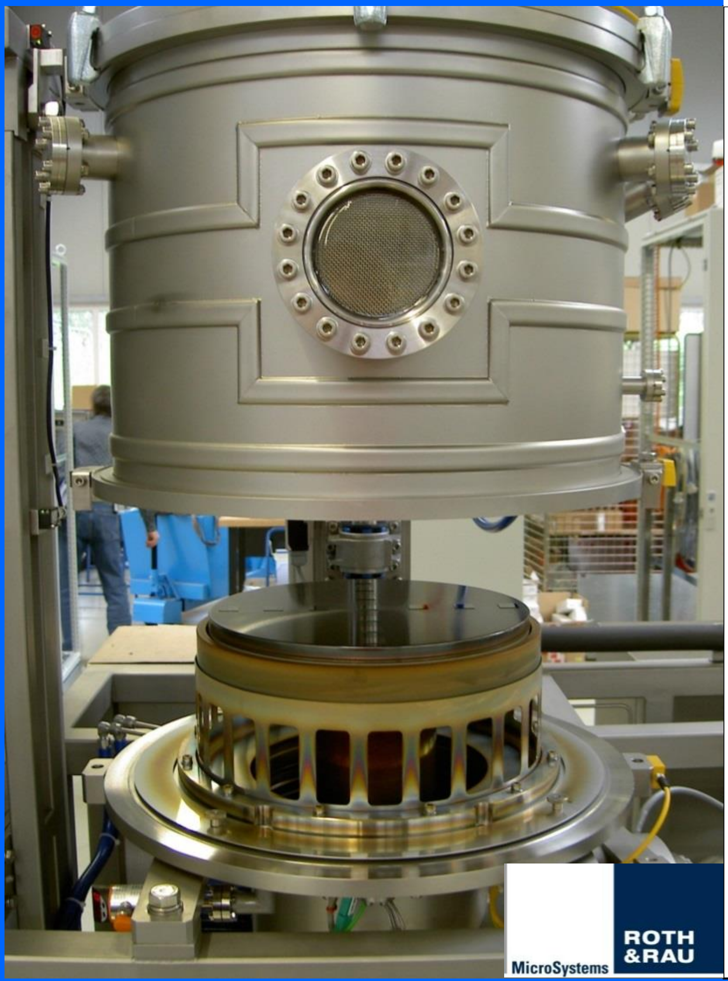


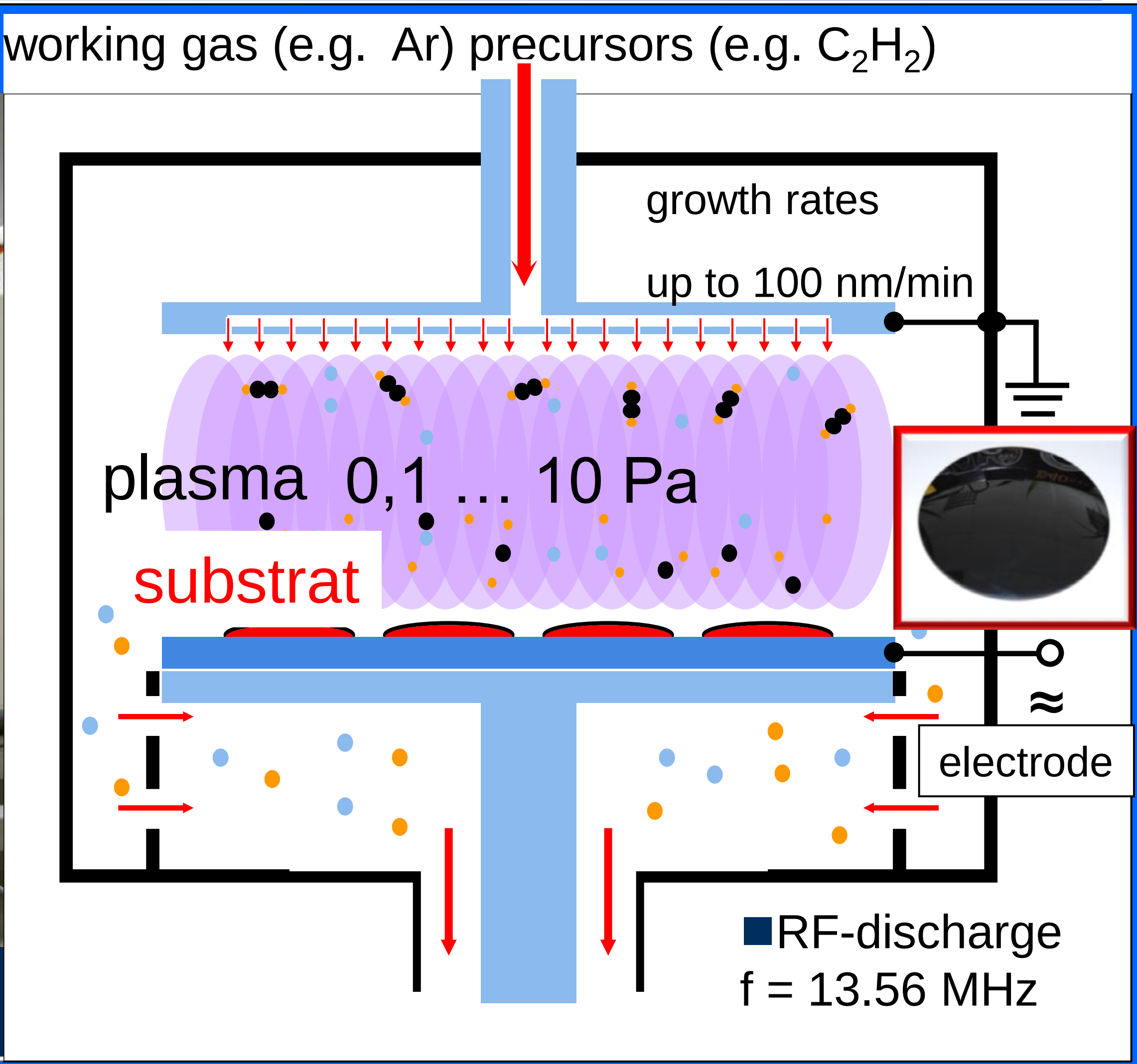
$$\left(\frac{V_1}{V_2} = \frac{A_2}{A_1}\right)^4$$



RF (AC) for DLC often:
High Frequency HF
13,56 MHz (HF: 3-30 MHz)
Medium Frequency MF
(300 kHz-3MHz) also
Low Frequency LF
30-300 kHz possible

PACVD for DLC by RF glow discharges: IR optics





H_V → 28 GPa/ refractive index n = 2.1/ film thickness 1150nm
density σ = 1.9 g/cm³/hydrogen content lower then 15 %

PACVD for DLC by RF glow discharges: gas barrier coatings

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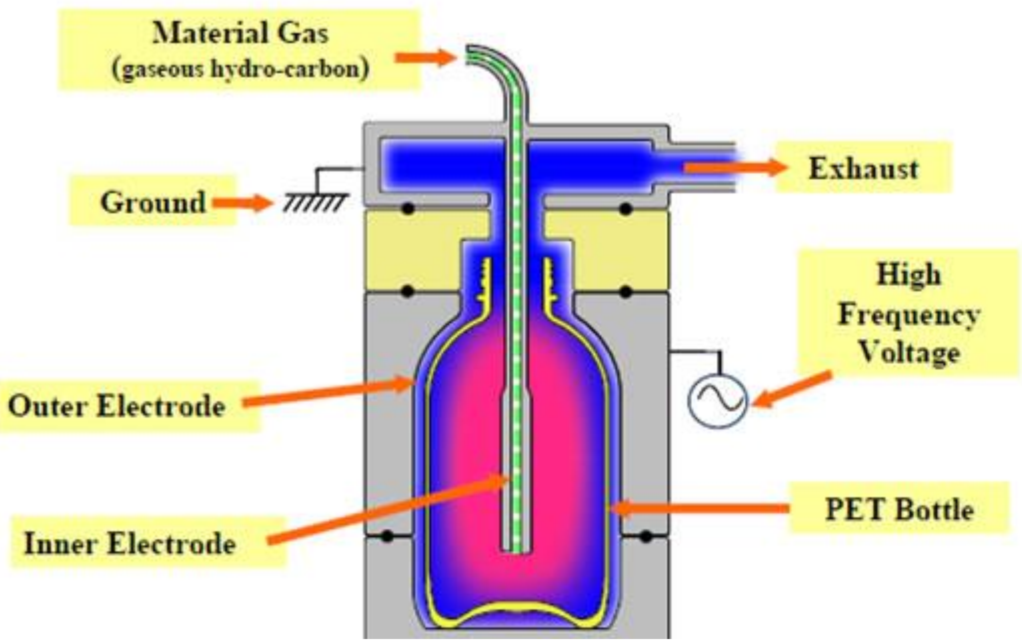


Mitsubishi Heavy Industries Technical Review Vol. 49 No. 4 (March 2012)

ATSUSHI UEDA[1] MASAAKI NAKACHI[2] SEIJI GOTO[2] HIDEO YAMAKOSHI[3] AKIRA SHIRAKURA[4]

Mitsubishi Heavy Industries, Ltd. Technical Review Vol. 42 No. 1 (Feb. 2005)

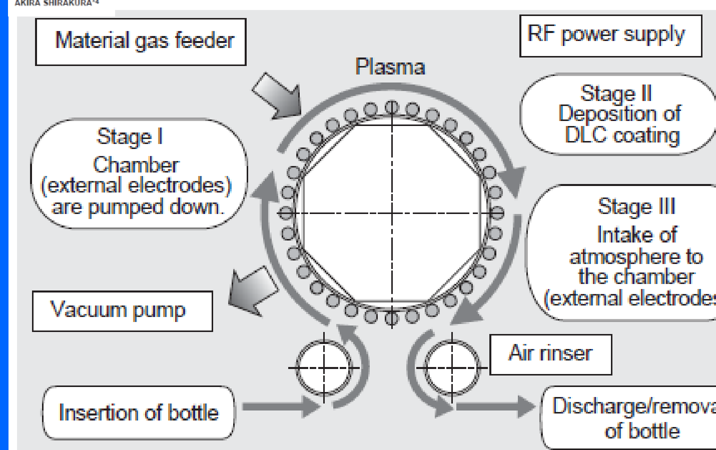
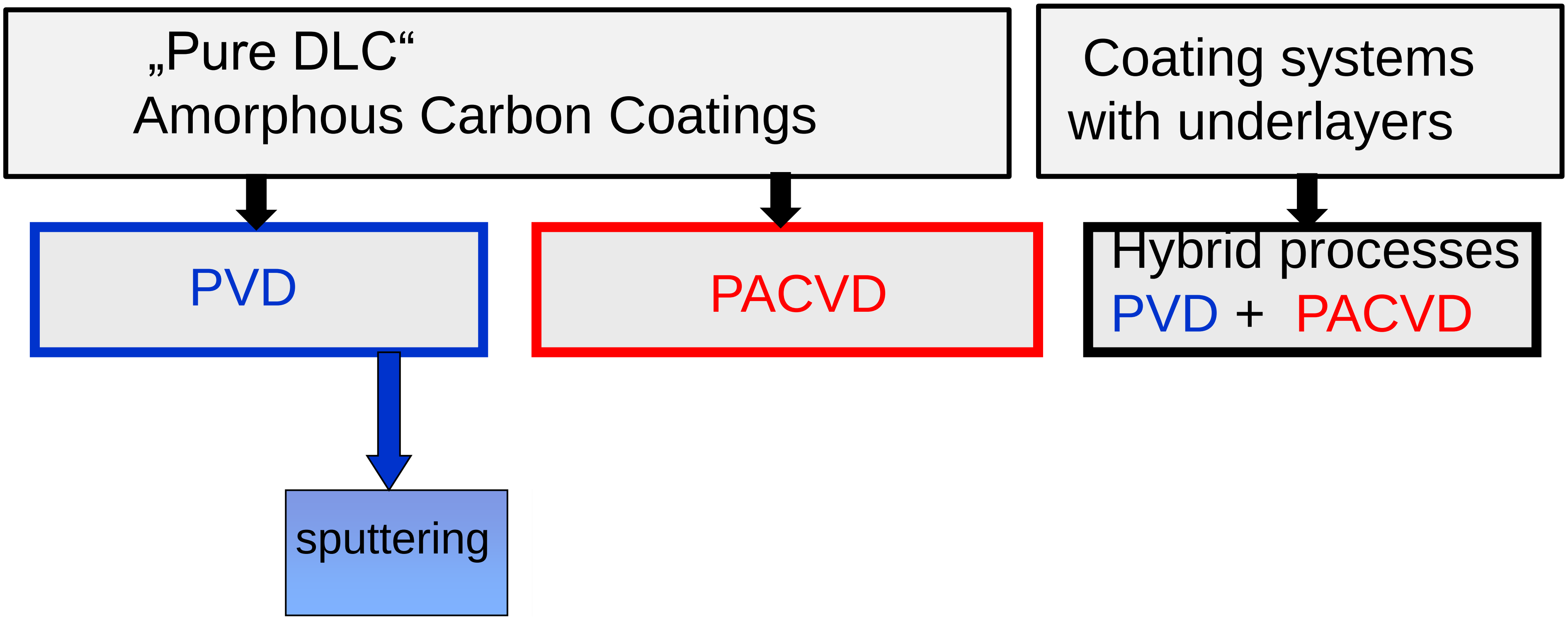


Fig. 2 DLC plasma coating process
Film-forming process of rotary DLC plasma coating system.

Most important industrial deposition methods for DLC coatings on 3D parts



DLC by sputtering: History – Highlights

Sulzer Metco

1984

[75] Inventors: **Akio Hiraki**, Nishinomiya; **Tatsuro Miyasato**, Osaka; **Masao Hayashi**, Wako, all of Japan

Sputtering graphite
+ CxHy/F
a-C:H and a-C:H:X, X =F

A lot of developments and applications recording media, hard discs

development of deposition methods

Development &
selected small scale application:
components, gears, tools

Industrial break through of a-C:H:W
Unit injector VW

Introduction:
Magnetron sputtering
+ PACVD

mass production

Sputtering Carbides!!!
Who where first?

1980 — 1985 — 1990 — 1995 — 2000 — 2005 — 2010

1982

A workpiece comprises a substrate having a sliding surface provided with a friction-reducing coating. Such coating consists essentially of elemental carbon dispersed in a matrix formed of at least one metallic element in the proportions of 50.1 to 99.1 at % of the elemental carbon and 0.1 to 49.9 at % of the metallic element. The ratio of the metallic element to the elemental carbon differs from the stoichiometric ratio of the carbide.

[54] CARBON-CONTAINING SLIDING LAYER
[75] Inventors: **Heinz Dimigen; Hubertus Hübsch**, both of Hamburg, Fed. Rep. of Germany

Sputtering Me or Si
a-C:H:Me (W, …)
a-C:H:X; X = Si

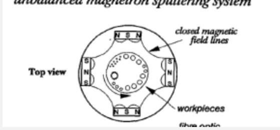
1993

JOURNAL DE PHYSIQUE IV
Colloque C3, supplément au Journal de Physique II, Volume 3, août 1993

Ion-assisted CVD of graded diamond like carbon (DLC) based coatings

D.P. MONAGHAN, D.G. TEER*, R.D. ARNELL**, I. EFEOGLU** and W. AHMED***

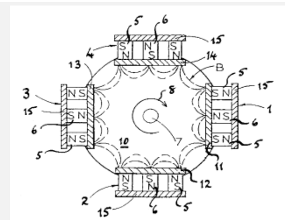
Schematic of a 4 magnetron closed field unbalanced magnetron sputtering system



Sputtering UBM/closed field
Sputtering graphite
+ CxHy
a-C:H:Ti/TiC
a-CH on top
Underlayer:
Ti/TiN/TiCN/TiC

1997

(75) Inventors: **Dennis Gerald Teer**, Worcestershire (GB); **Didier Camino**, Anoye (FR); **Andrew H S Jones**, Shropshire (GB)



2. An article bearing a carbon-containing coating, wherein said coating comprises a succession of carbon and metal-containing layers, wherein the carbon-containing layers

Sputtering UBM/closed field
Sputtering graphite
´sputtering metal (Cr)

2003

HiPIMS/HPPMS
For DLC ???

B.M. DeKoven et.al.
Carbon Thin Film Deposition
Using HPPMS,
46th Ann.Techn.Conf.Proc, SVC,
San Francisco, CA 2003

2006

„C-DLC" FhG IST
Optimized C-sputtering
plus CxHy

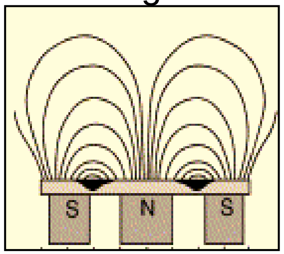
1976 first C sputtering:
Z. Marinkovic, R. Roy
Carbon, Vol 14, 329
„Glassy" carbon

Dr. Jörg Vetter, ICMCTF2013

Sputtering DLC: magnetrons and system configurations

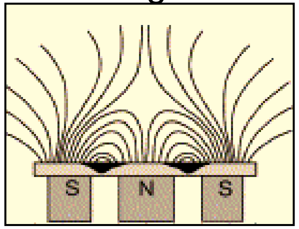
Sulzer Metco

BM magnetrons



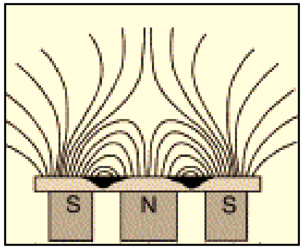
weak magetic field
near the substrates

UBM magnetrons



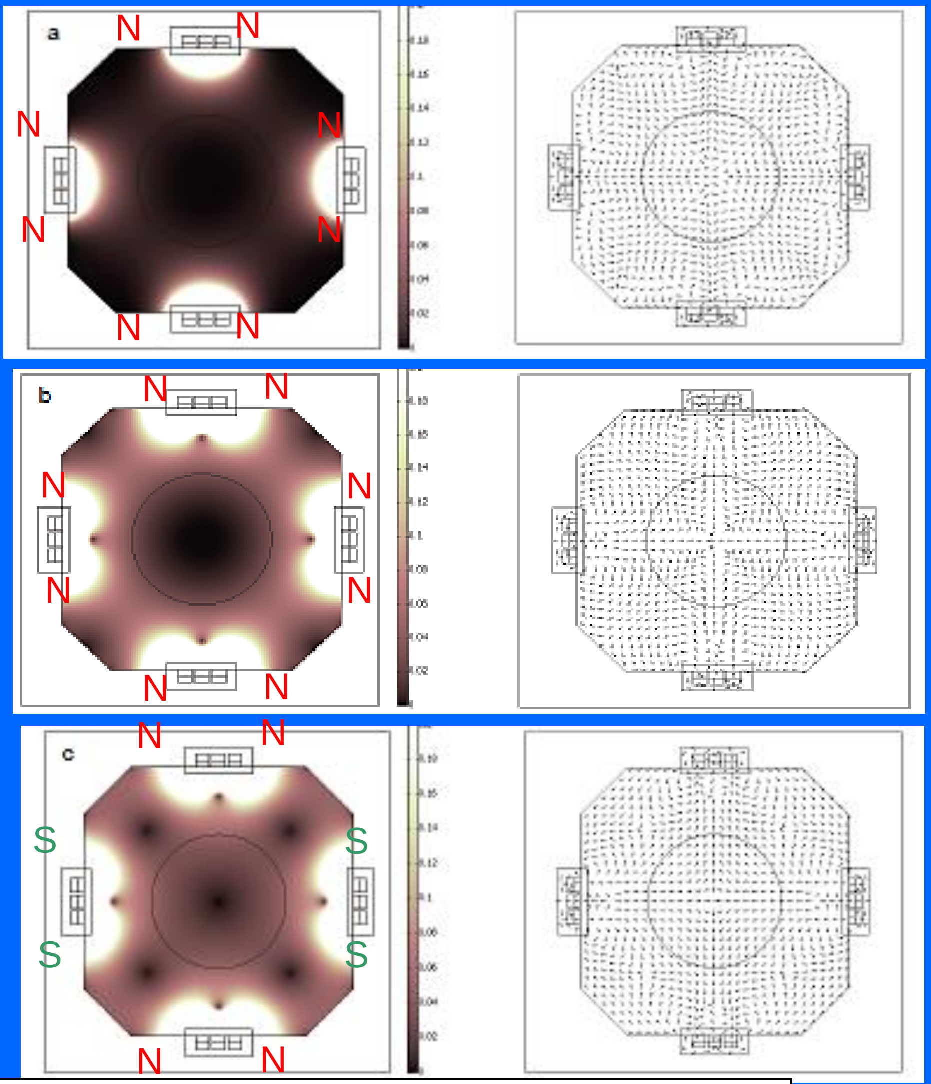
stronger magnetic field
near the substrates,
higher plasma density

UBM magnetrons



closed field:
highest plasma density
- „full“chamber
- face-to-face couples
(cross field).

2D finite element modeling (FEM): 0 – 0,2 mT



Dominating in application: UBM and different closed field configuration, DC and pulsed DC

Use of graphite targets
DC / pulsed DC / RF / HiPIMS

non-reactive sputtering

a-C (ta-C?)
carbon coatings
⇩
acustic/
loudspeakers

a-C/Me
multilayers
⇩
e.g.
tribological
a-C/Cr

„Mixed“ targets
graphite
plus Me/Si

reactive sputtering / PACVD?

a-C:H
H from gas
⇩
main use
for
classical
tribological
applications

a-C:H:X
H, X from gas
⇩
X : Si, F ….
used for
modificat.
Si: temp. stab.
F: wetting

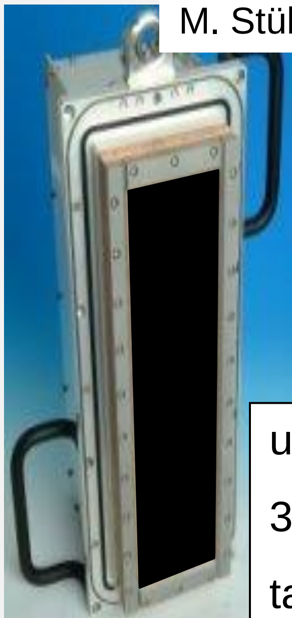
a-C:N
N from gas
⇩
used
for
hard disk
overcoat

Hard a-C (H) coatings by magnetron sputtering for 3 D parts – rotation effects

SULZER
Sulzer Metco

Effects in UBM DC sputtering of hard a-C on 3D parts

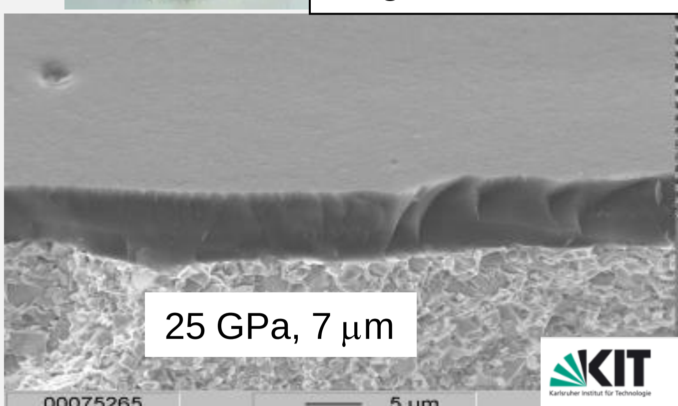
M. Stüber, J. Vetter 2008



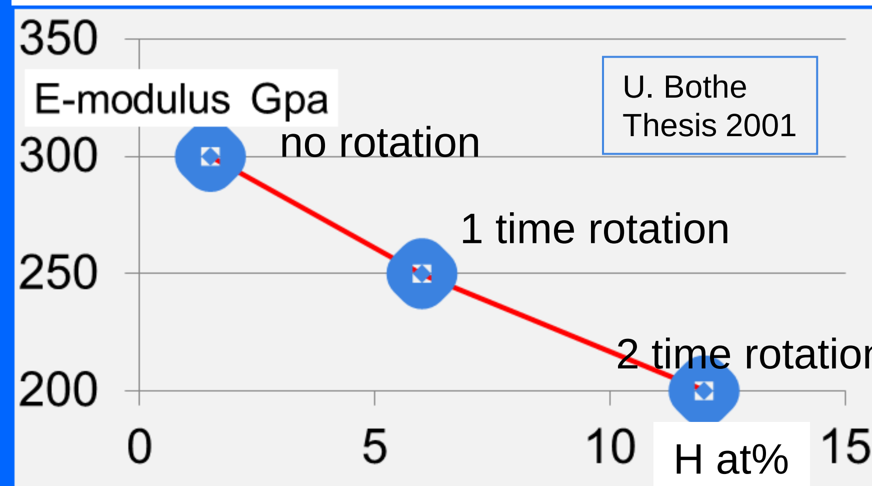
upscaled process

3-fold rotation

target: 4 W/cm²



Rotation effect:
Hydrogen and E-modulus



Possible to make thicker tribological coatings:
- low deposition rates,
- difficult to make high hardness /sp³ content
- 3D parts: H content – rotation effects

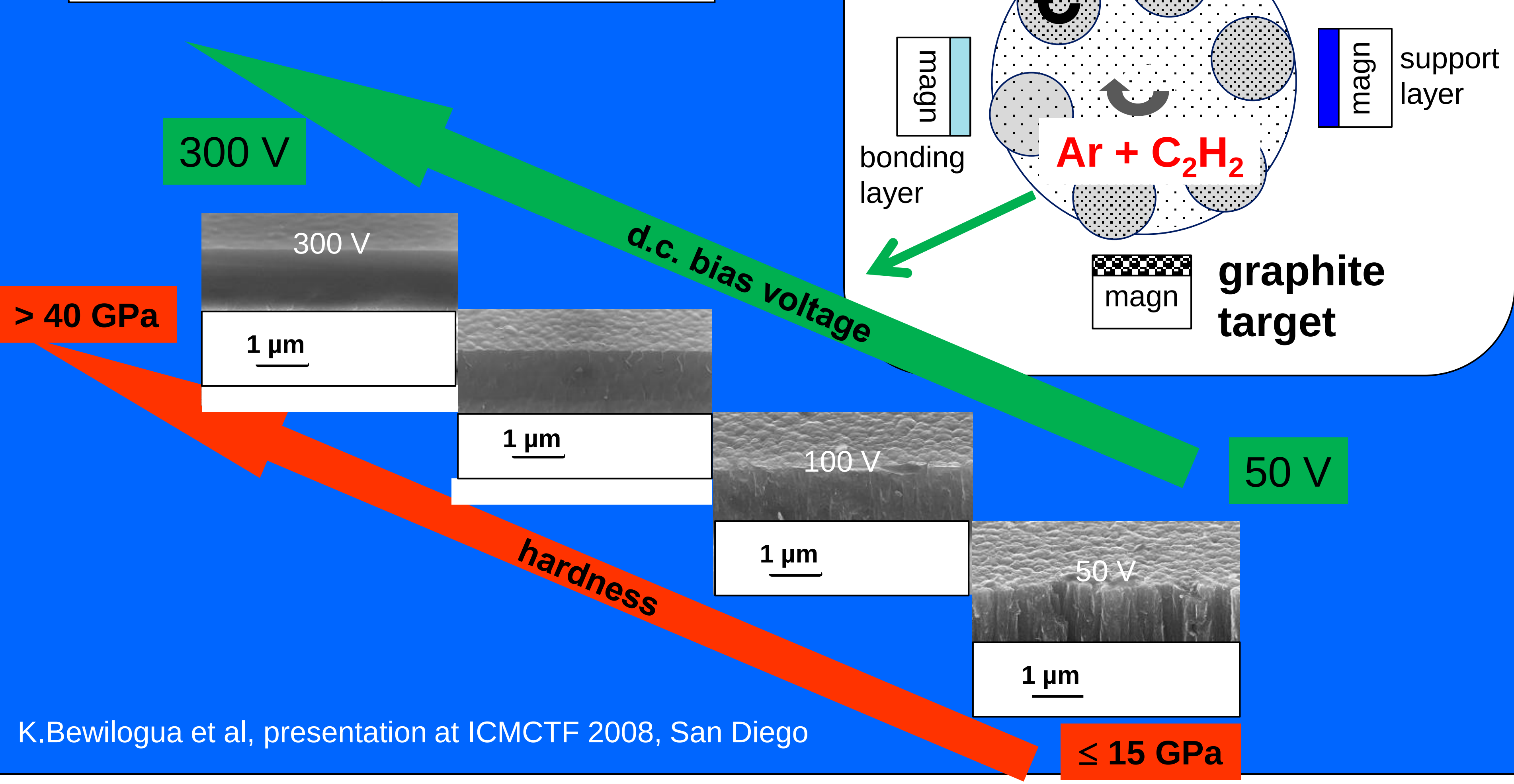
If we have always H in, why not running with CxHy?

Sputtering DLC: a-C:H:X coatings for 3D parts

Use of graphit targets plus carbon gas: reactive sputtering

reactive sputtering

$C(target) + C_xH_y\ (gas) \Longrightarrow a\text{-}C{:}H$



K.Bewilogua et al, presentation at ICMCTF 2008, San Diego

DLC by HiPIMS: what can be done by High Current Pulsed MS? (not in industrial use)

SULZER

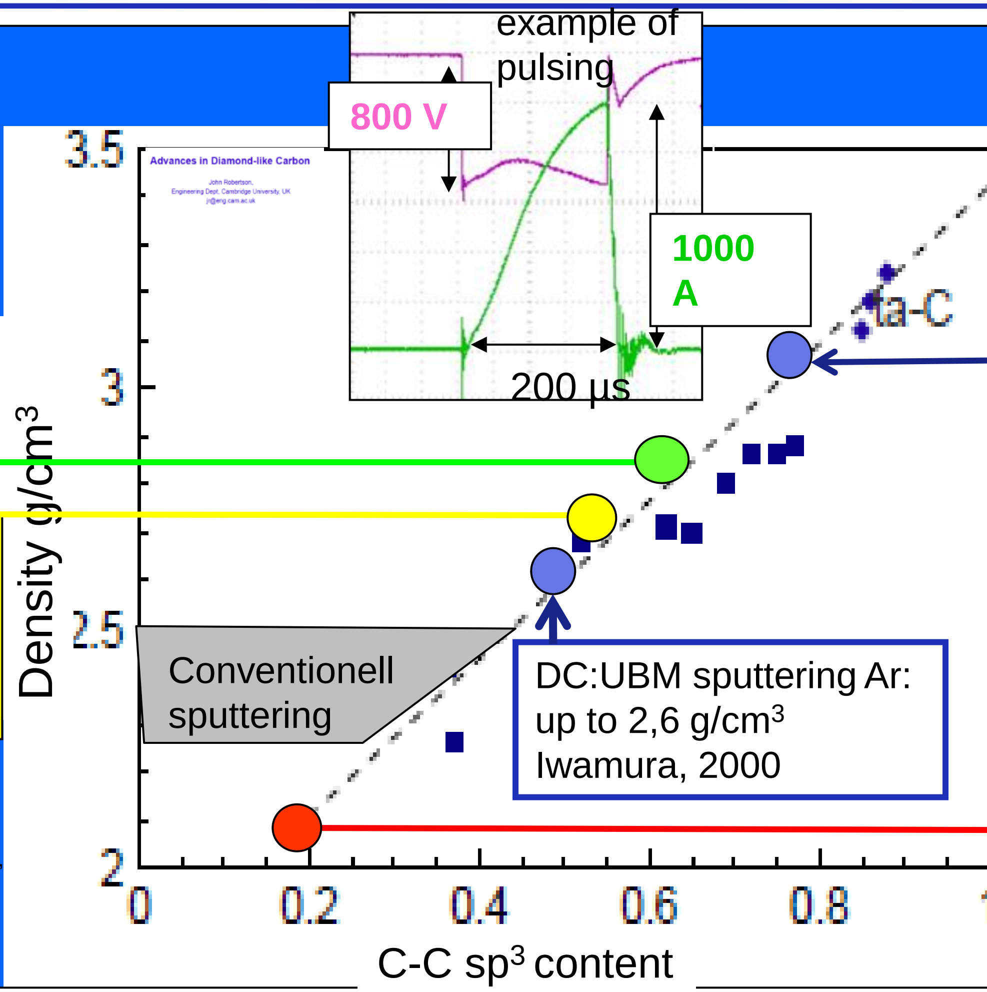
Sulzer Metco

A. Ajaz et.al.
A strategy for increased carbon ionization in magnetron sputtering discharges
Diamond &Related Materials 23(2012)1-4

2012 Neon HiPIMS
Carbon film density
up to 2,8 g/cm³
H: 5-10 at%

2003 Argon HiPIMS
Carbon film density
up to 2,7 g/cm³
H: ???

B.M. DeKoven et.al.
Carbon Thin Film Deposition Using High power Pulsed Magnetron Sputtering,
46th Ann.Techn.Conf.Proc, SVC,
San Francisco, CA 2003



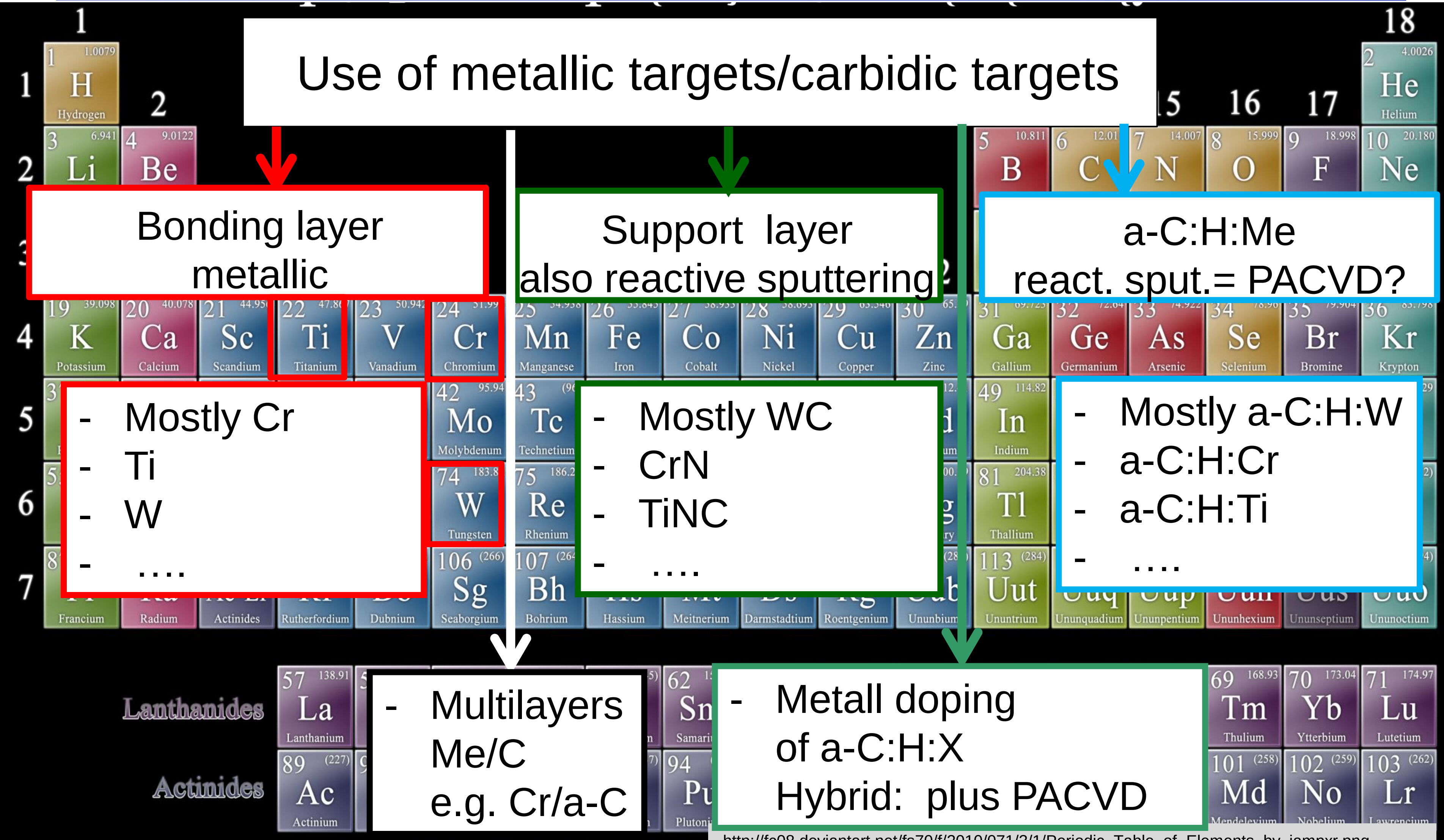
S. Nakao et. al.
Effect of Ar gas pressure on microstructure of DLC films Deposited by high-power pulsed magnetron sputtering
Vacuum 89 (2013)261

2013 Argon HiPIMS
Carbon film density
up to 2,03 g/cm³
H: 10 at%

C⁺/C-ratio also low for HiPIMS: means the Ar⁺ bombardement is of importance

α,β,γ < 1 no sustained self-sputtering possible:
no HiPIMS effect – only High Current Pulsed Discharge

Sputtering of tribological DLC coatings for 3D parts



Use of metallic targets/carbidic targets

Bonding layer metallic

- Mostly Cr
- Ti
- W
- ….

Support layer also reactive sputtering

- Mostly WC
- CrN
- TiNC
- ….

a-C:H:Me react. sput.= PACVD?

- Mostly a-C:H:W
- a-C:H:Cr
- a-C:H:Ti
- ….

- Multilayers Me/C e.g. Cr/a-C

- Metall doping of a-C:H:X Hybrid: plus PACVD

http://fc08.deviantart.net/fs70/f/2010/071/3/1/Periodic_Table_of_Elements_by_iampxr.png

SULZER: Example: use of metallic targets: Cr and WC

a-C:H:Me: reactive magnetron sputtering

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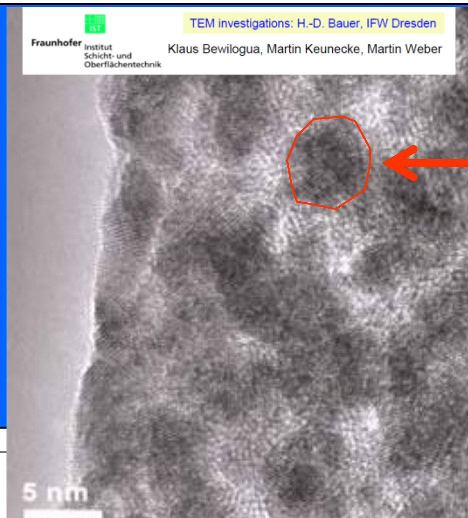
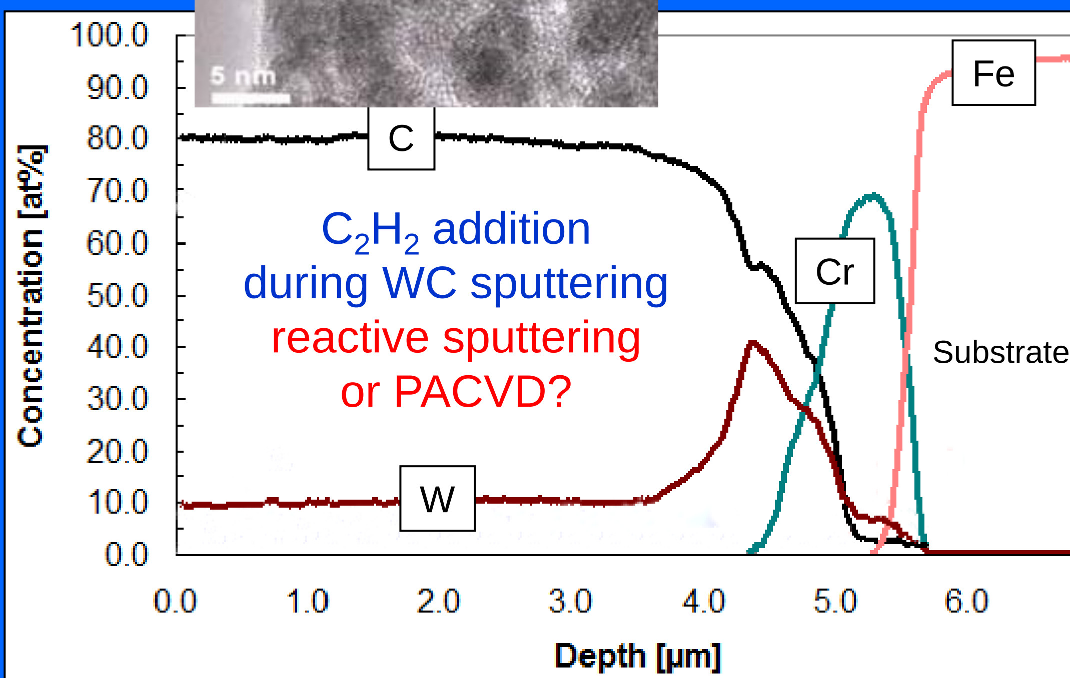
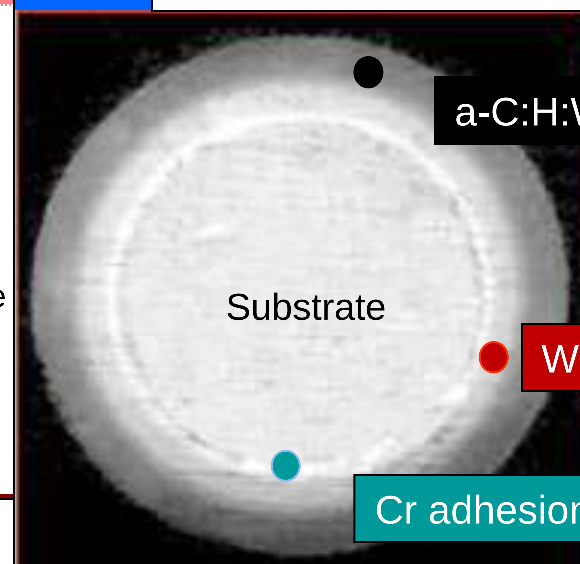
Most important coating type: sputtering using metallic targets

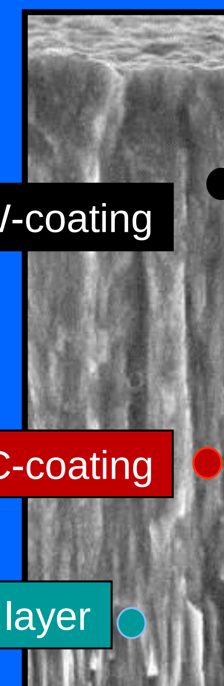


a-C:H:W
WCx crystalls
in a-C:H matrix

patent 1982: **a-C:H:Me**
Prof. Dr. Heinz Dimigen







SULZER: Up scaling of DLC coaters for large size parts

a-C:H:Me and hybrid plus a-C:H:X

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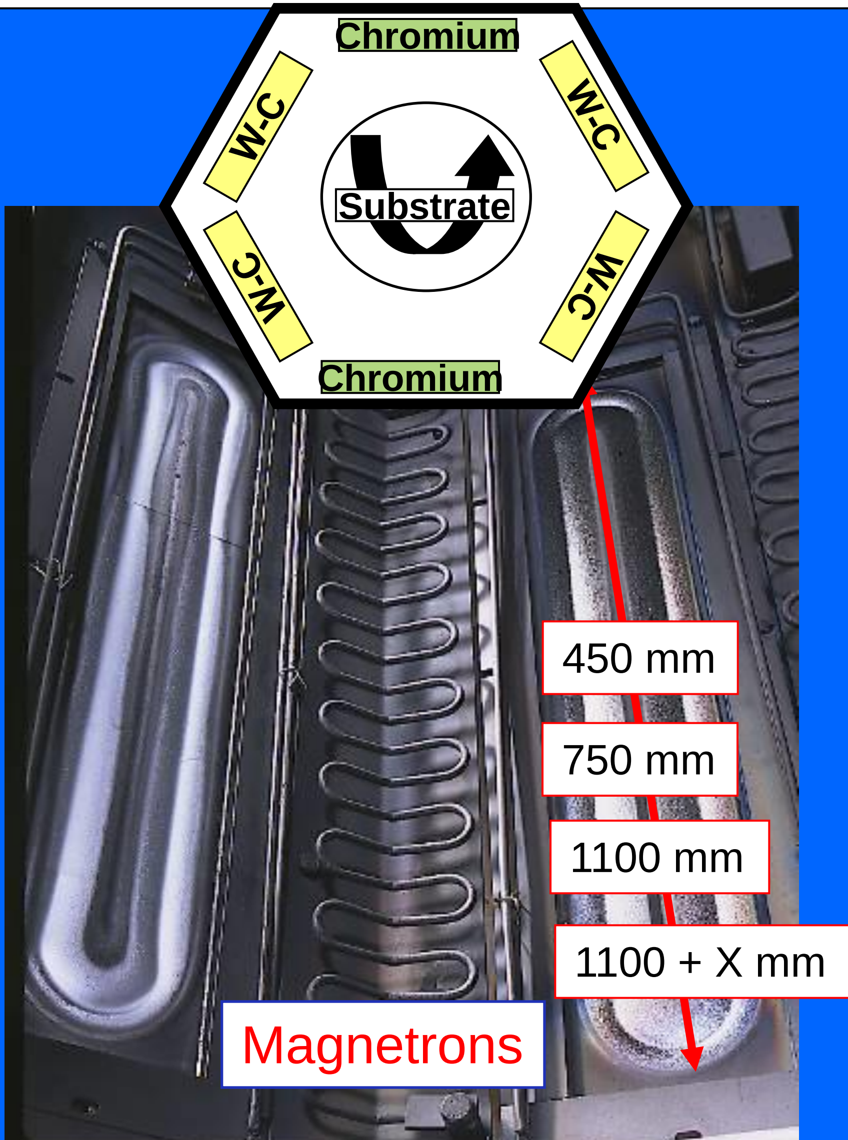

Double rotating gear parts

Large pinion shaft

SULZER: DLC doping by sputtering + PACVD

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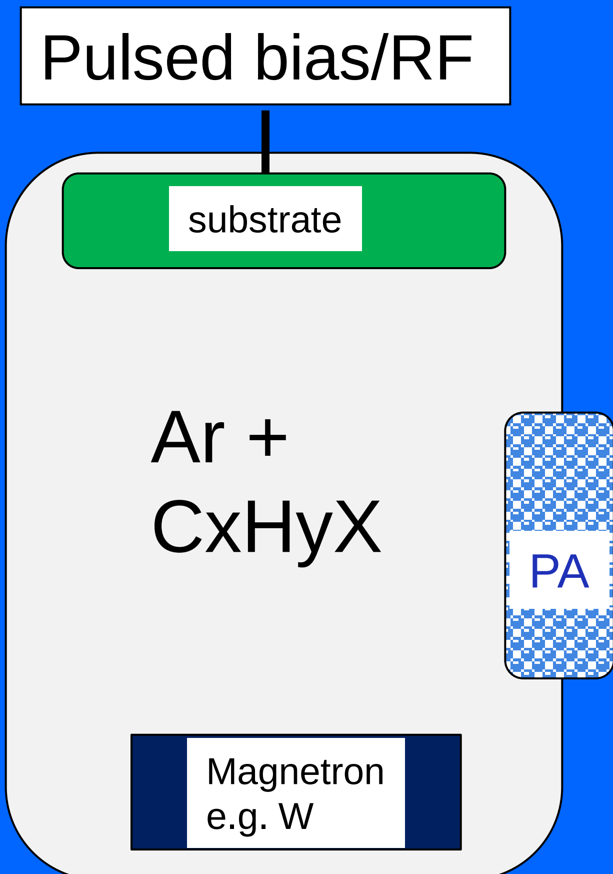
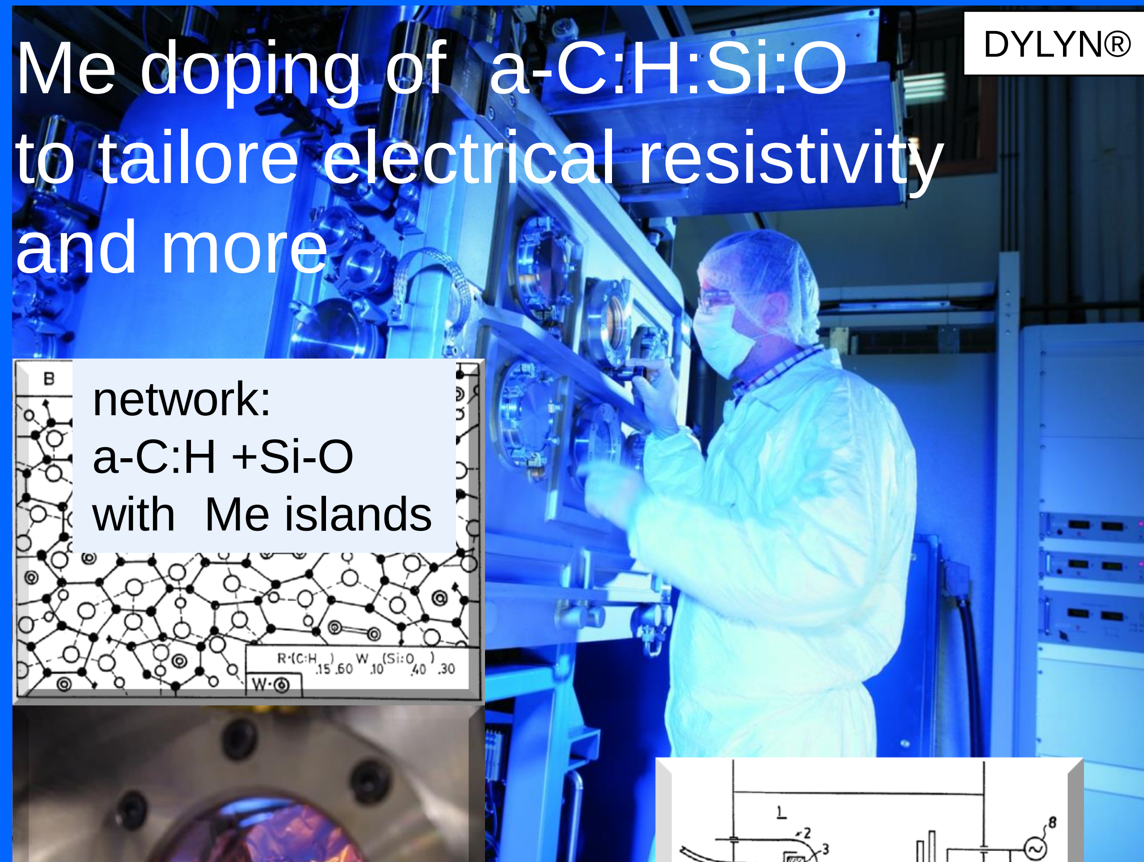
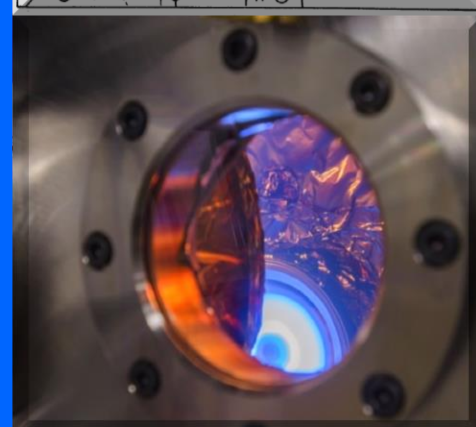


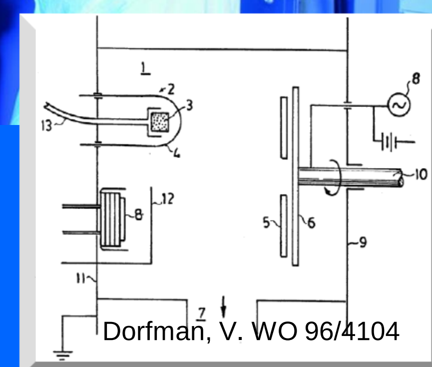
PA :
hot filament
plasma source



Me doping of a-C:H:Si:O
to tailore electrical resistivity
and more

network:
a-C:H +Si-O
with Me islands





Most important industrial deposition methods for DLC coatings on 3D parts

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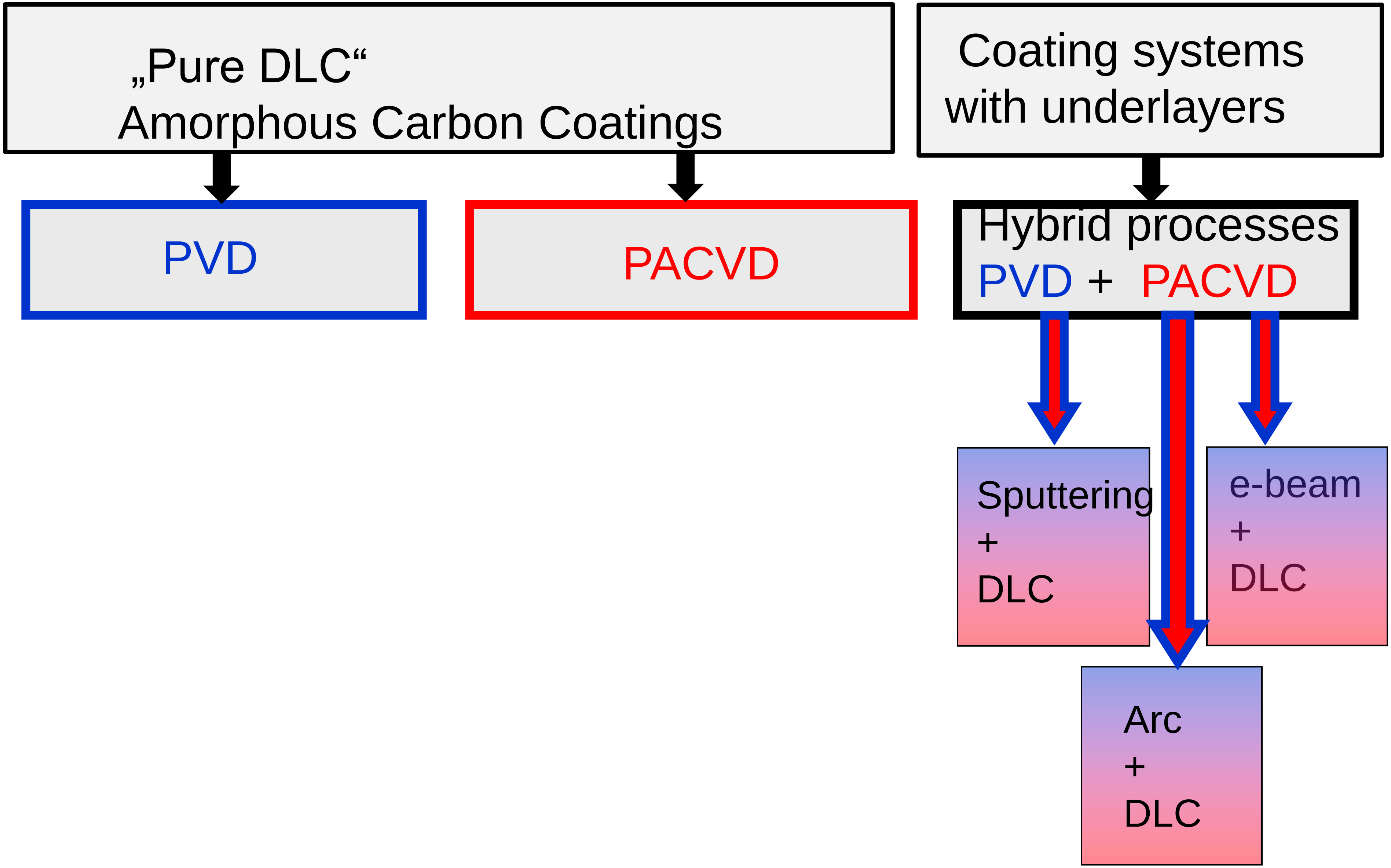

Some important coating architectures in hybrid processes: Top functional coating always a DLC-type

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"pure" DLC-type coatings

"homogenous" DLC-type coating

structural gradient or ml DLC-type coating

composit. gradient or ml DLC-type coating

a-C:H:X
nano-composite
e.g. a-C:H:Si:O
Example

a-C(H)
high sp^3
Example
low sp^3

a-C:H
Example
a-C:H:X

DLC-type coatings on adhesion/support layers

The tailored architecture: often the gate for the performance !

DLC-type
thin non DLC adhesion layers e.g. Ti

DLC-type
thick non DLC support/ adhesion layers e.g. WC

Most important industrial deposition methods for DLC coatings on 3D parts

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„Pure DLC“
Amorphous Carbon Coatings

Coating systems with underlayers

PVD

PACVD

Hybrid processes
PVD + PACVD

Sputtering
+
DLC

SULZER: DLC by Hybrid: Sputtering + PACVD for 3D parts
: adhesion layer for a-C:H:X, e.g Ti by rotatable magnetron

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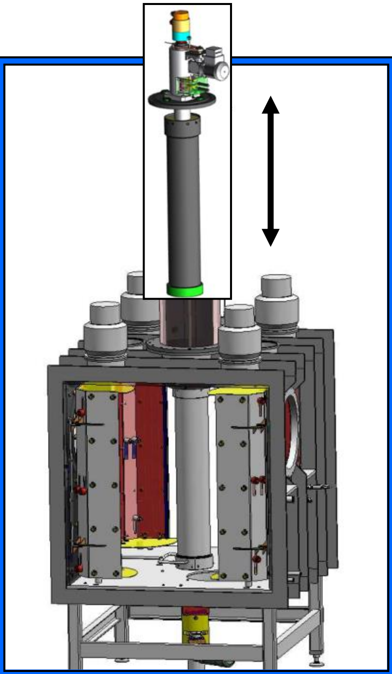
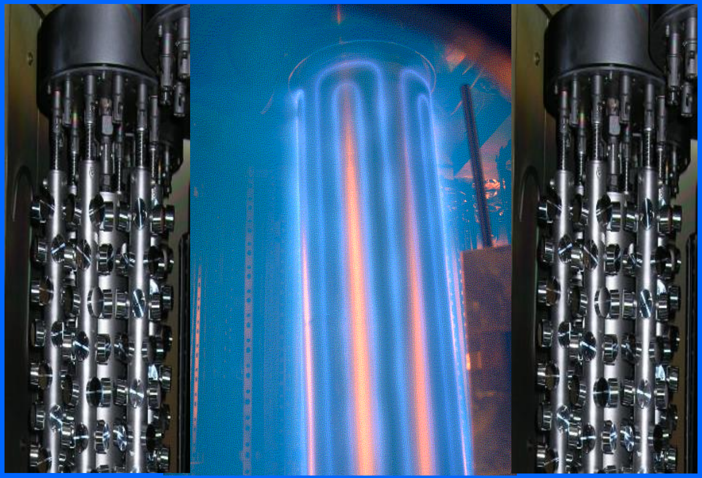
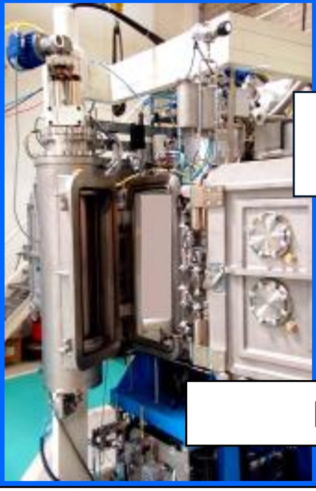
DYLYN®Plus

Coating zone:
height about 1 m

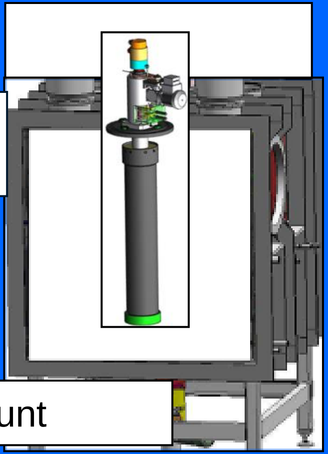


Rotatable: central mount





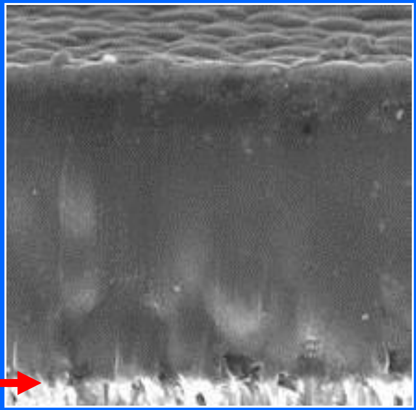
Coating zone:
height about 0,6 m



Rotatable: side mount

a-C:H/
a-C:H:Si:O

sputtered
adhesion layer



SULZER: DLC by Hybrid: Sputtering + PACVD for 3D parts
: adhesion/support layers for a-C:H:X by sputtering

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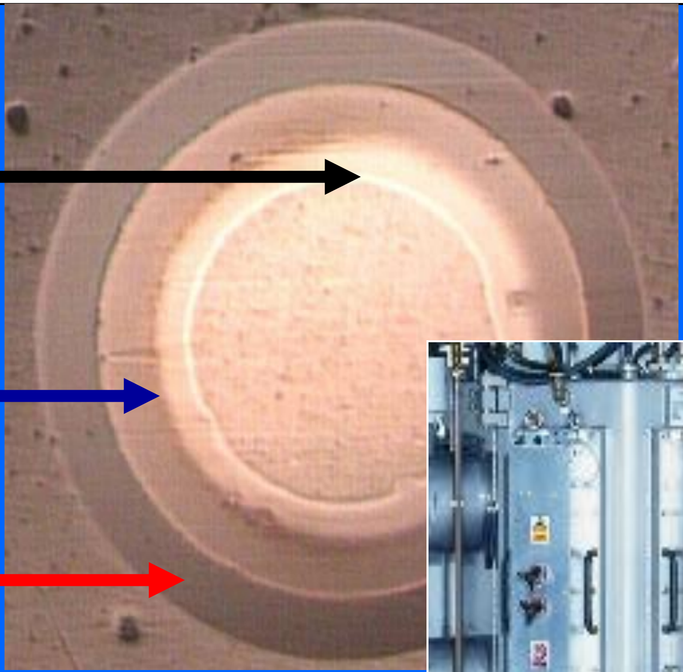
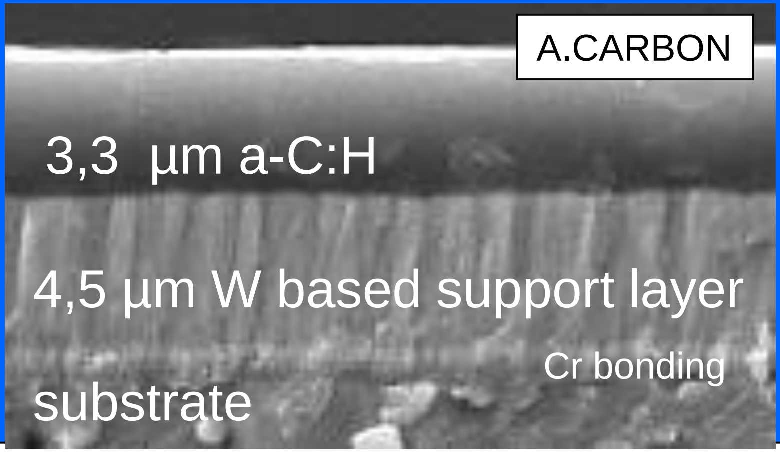
1) Sputtering bonding/support
metal/nitrides/carbonitrides.g.
Cr/Cr_2N/CrN/CrNC

2) Sputtering a-C:H:Me
e.g. sputtering WC plus C_2H_2
= a-C:H:W

3) PACVD
e.g pulsed glow discharge
= a-C:H:X





Most important industrial deposition methods for DLC coatings on 3D parts

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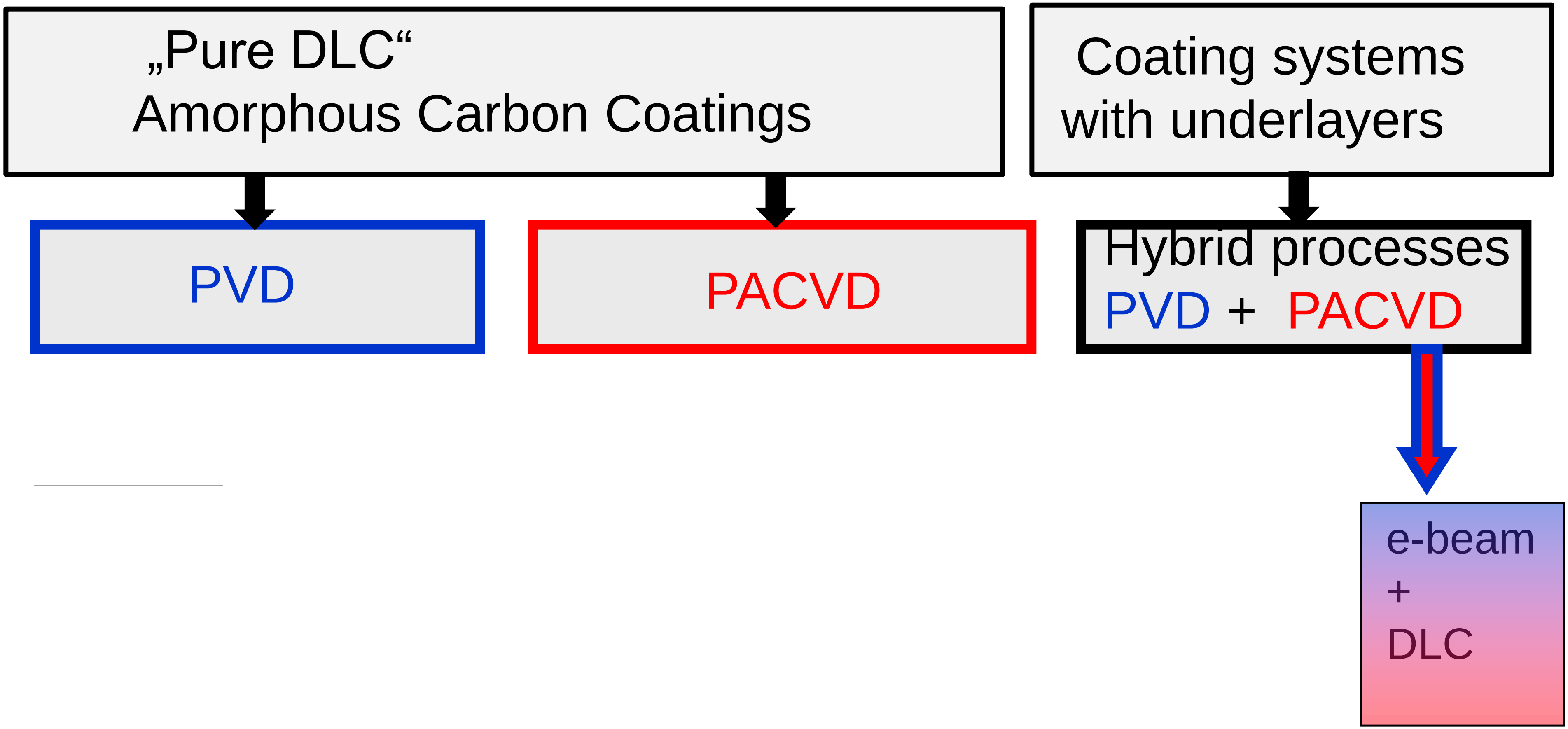

SULZER: DLC by Hybrid: e-beam + PACVD for 3D parts
: adhesion/support layers for a-C:H:X by e-beam

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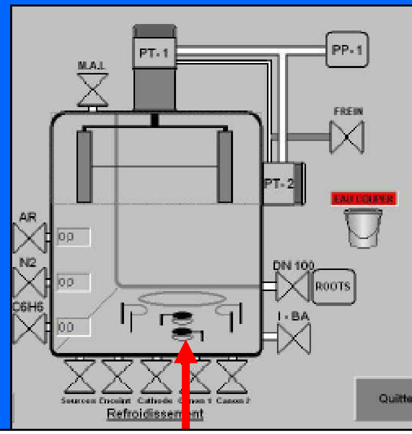
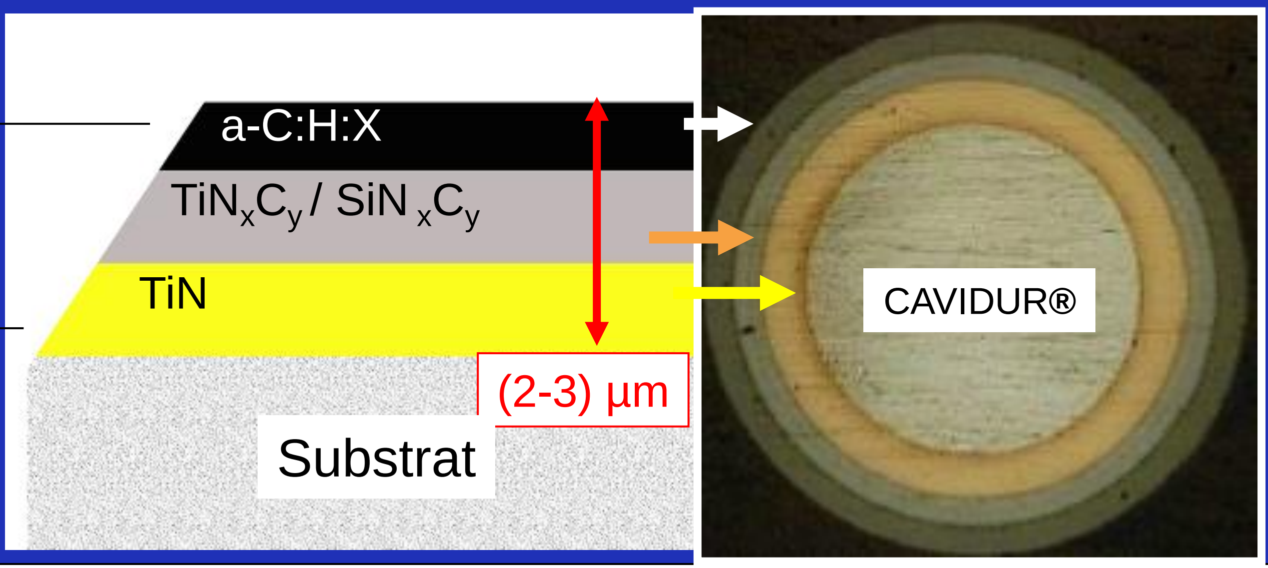
Loading room
"clean room"



e-beam evaporator:
smooth and dence underlayer

Deloading room
"operation room"

support/
adhesion
layer
by e-beam



Most important industrial deposition methods for DLC coatings on 3D parts

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„Pure DLC“
Amorphous Carbon Coatings

Coating systems with underlayers

PVD

PACVD

Hybrid processes
PVD + PACVD

Arc
+
DLC

SULZER: DLC by Hybrid: arc + sputtering
Functional top layer on arc-PVD coatings

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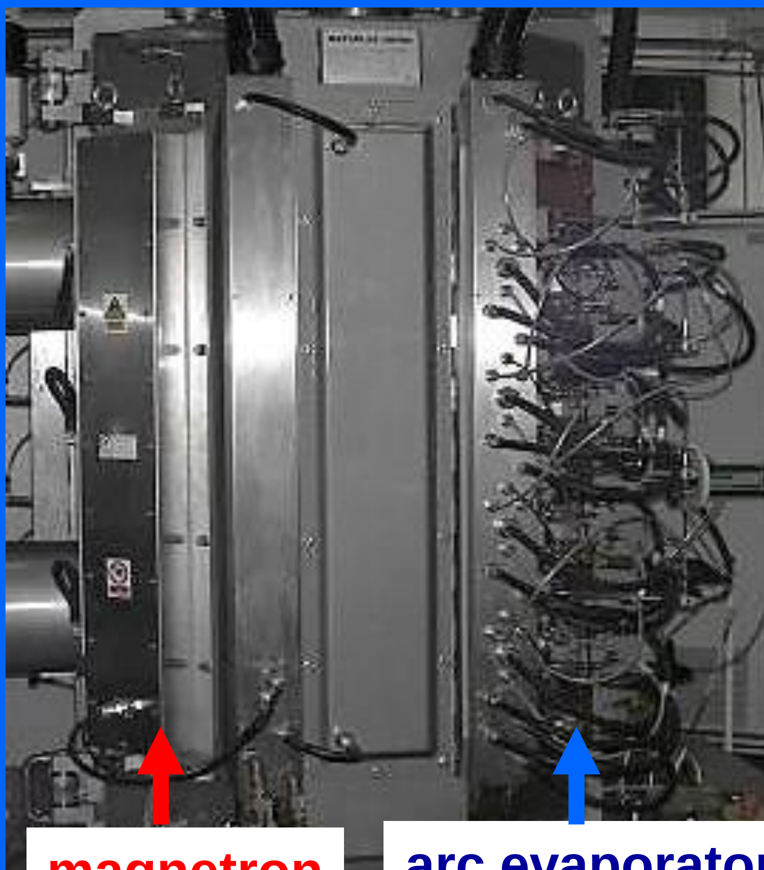

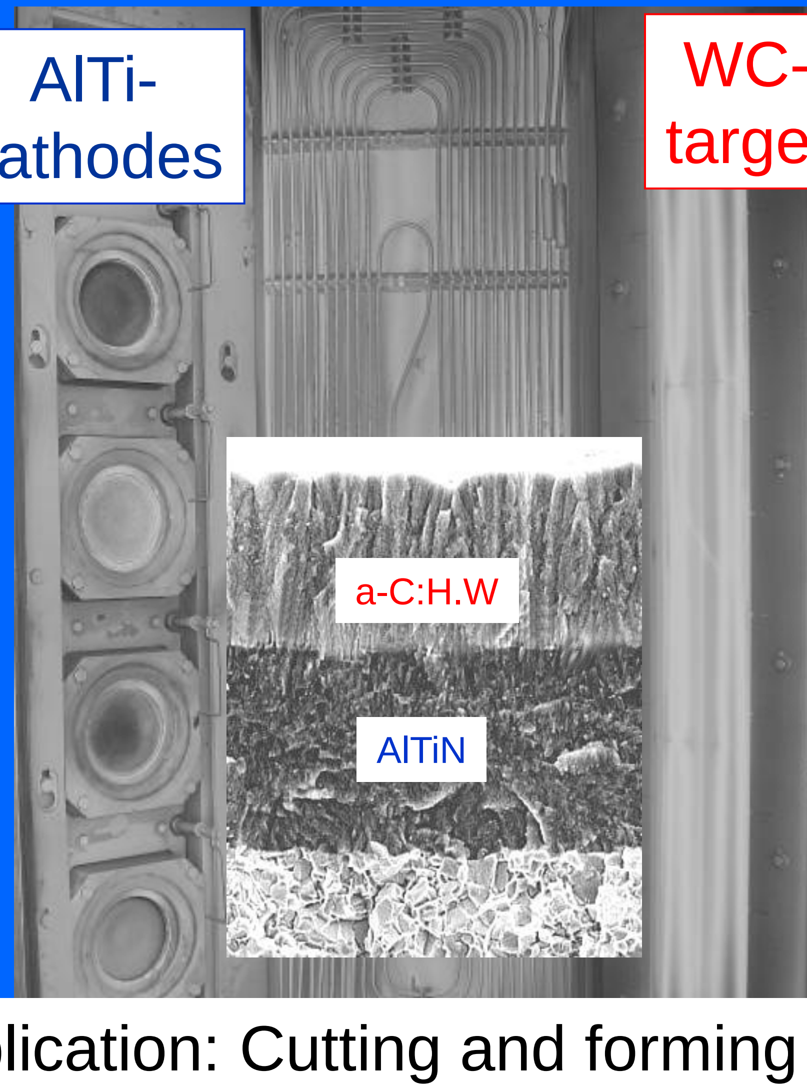

Application: Cutting and forming tools

7. Summary and Outlook: 7.1. “pure” DLC-coatings

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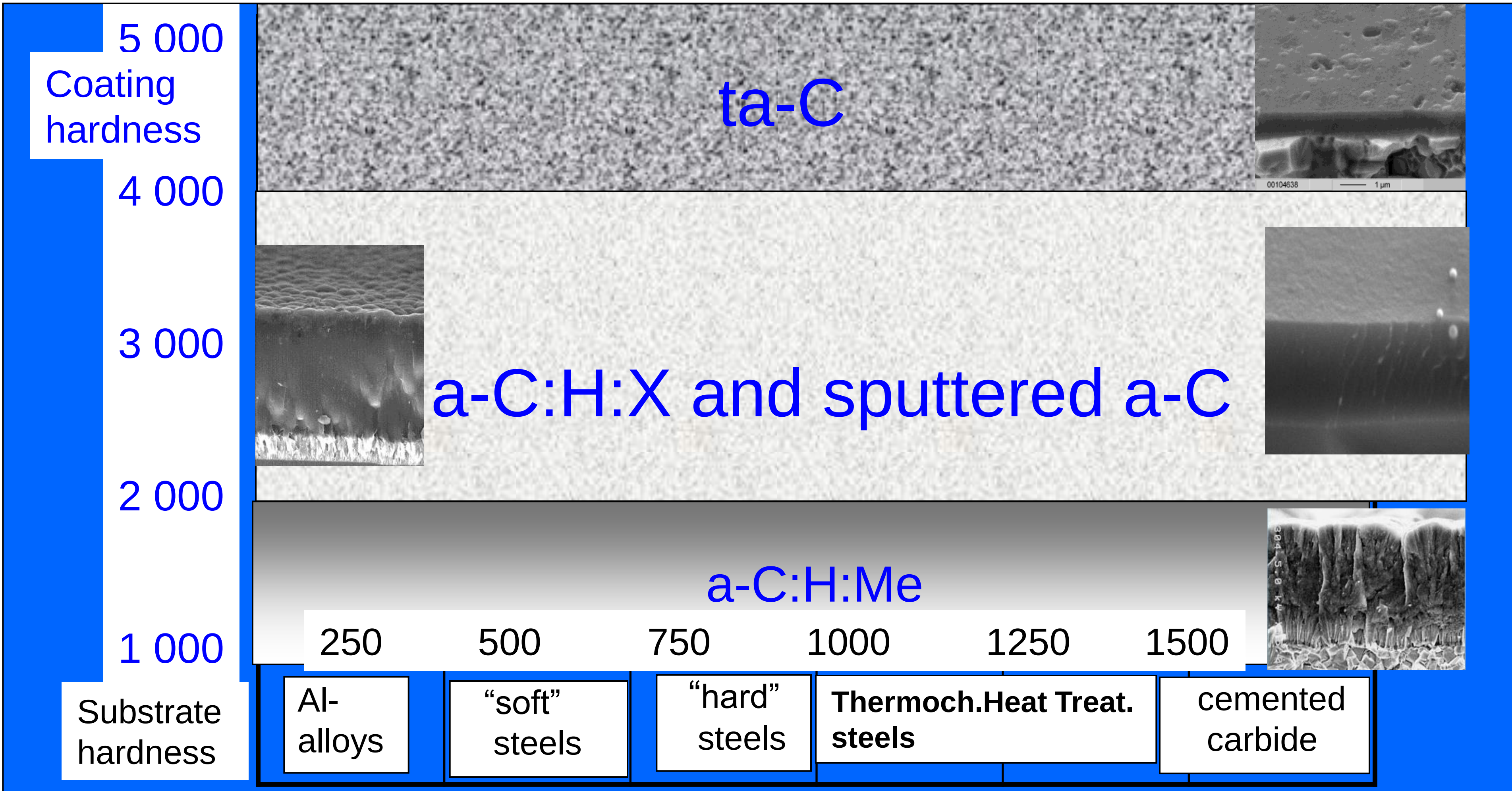
Q.: Which is the best DLC coating/ deposition method?
rate, costs, performance and …. ?

A.: All ! Its application driven: coating properties, parts (geometry material),tribosystem …



7. Summary and Outlook: 7.2: Coating architectures/deposition methods within one service provider is large! (example Sulzer Thin Film Group)

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Deposition method	PACVD	Magnetron -sputtering + PACVD		Magnetron -sputtering	e-beam evaporat. + PA-CVD	arc evaporation of the base layer plus magnetron Sputtering for DLC and/or PA-CVD
Coating architecture	a-C:H:X nano-composite a-C:H:Si:O	Me + a-C:H:X	Me(C/N) + a-C:H	a-C:H:Me	Me/Si(N/C) + a-C:H a-C:H:X	
Commercial name of coating	DYLYN®	DYLYN® plus	A.CARBON	WCH	CAVIDUR®	

7. Summary and Outlook: 7.3: general remarks

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1. UBM Sputtering (closed field configurations) is the main deposition method for thicker coatings (several µm) in tribological applications.
Besides the **a-C:H:Me** coating also of **a-C:H:X** coatings
by graphite sputtering plus a carbon gas (CxHy:X) are more and more in use.
One driver in automotive applications is the goal to reduce the CO2 emission of cars.

2. PACVD to deposit **a-C:H:X** for thick tribological coatings are mostly based *on the Pulsed Glow Discharges (without or with an additional plasma source).*
Ion sources (e.g. anode layer) are suitable for large area coatings.
Mircowave and RF discharges are also used to deposit thin gas barriers for "beer" bottles.

3. Vacuum Arc Evaporation (direct/filtered) with constant or pulsed current is applied to deposit **ta-C** coatings for hard disks, but also for tools and automotive applications.

4. Industrial Hyprid processes = PVD + PACVD based on PVD processes, (sputtering, e-beam, arc) to deposit adhesion and support layers under the functional DLC (a-C:H:X) coatings are the dominating deposition methods for thicker tribological coatings (e.g. automotive applications).

.....

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5. The DLC coatings and the deposition methods don’t go to pension after 60 years …

DLC is still the

for the solution of a lot of tribological problems.

Thanks for following me and listening !