

Amorphe Kohlenstoffschichten und deren Eignung als biofunktionale Oberflächen

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311001

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Outline



- > relevance of amorphous and diamondlike carbon coatings
- > DLC coatings some fundamental aspects
- DLC coatings from R&D level to industrial production
- DLC coatings future challenges

Applications in medicine and pharmacy ...









urology: catheter (OptiMed Medizinische Instrumente GmbH)



one way syringe (Sulzer Metaplas)



chirurgical instruments (Plascotec GmbH)

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cardiovascular valve (St.Jude Medical)

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tabletting tool (Notter GmbH)

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... applications in engineering





G. van der Kolk, IonBond AG, PSE 2006



Rübig GmbH



Carbon materials – bulk and thin films





Classification of amorphous carbon coatings



Ternary phase diagram of bonding states in amorphous carbon and carbon-hydrogen materials

Variations of the sp²/(sp²+sp³) ratio versus the density of DLC films



J.Robertson, Mat. Sci. Eng. R 37 (2002) 129 A.C.Ferrari, J.Robertson, Phys. Rev. B 61 (2000) 14095 W.Jacob, W.Möller, Appl. Phys. Lett. 63 (1993) 1771 A.Saikubo et al., Diam. Rel. Mat. 17 (2008) 1743



Classification of amorphous carbon coatings





Synthesis of amorphous carbon coatings





Synthesis of amorphous carbon coatings

d.c.







- non-equilibrium process
- low temperature
- no ions
- low deposition rate
- low particle energies

cathodic arc evaporation



- non-equilibrium process
- low temperature
- 100% ions
- high deposition rate
- high particle energies

plasma assisted CVD



- equilibrium process
- higher temperature
- molecules, radicals
- high deposition rate
- various particle energies

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DLC synthesis – materials science point of view



DLC = amorphous carbon material with a significant fraction of sp^3 bonds

A.C.Ferrari, J.Robertson, Phys. Rev. B 61 (2000) 14095

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DLC synthesis – materials science point of view



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A.C.Ferrari, J.Robertson, Phys. Rev. B 61 (2000) 14095

gas pressure, gas flow cathode power densities substrate temperature substrate bias sample rotation distance source-substrate cathode material substrate material

plasma deposition control for DLC growth by PVD

DLC synthesis – materials science point of view



DLC = amorphous carbon material with a significant fraction of sp^3 bonds

A.C.Ferrari, J.Robertson, Phys. Rev. B 61 (2000) 14095



Scale-up of magnetron sputtering processes



laboratory scale Leybold Z 550 targets < 150 mm











Aspects of DLC synthesis at production scale







Diamor® - superhard carbon films by Laser-Arc deposition



physical / chemical properties

composition	nearly 100% carbon, < 1 at% H
density	2.4 – 3.2 g/cm ³
electr. resistivity	10 ³ – 10 ⁶ Wcm
refraction index	2.5 (at 700 nm wave length)
chem. resistance	inert (not against oxidising media and iron metals at elevated temp.)

mechanical / tribological properties

Young's modulus	400 – 650 GPa
hardness	40 – 65 GPa
coefficient of friction	0.10 – 0.15 (against steel under dry sliding conditions)

Laser-Arco® and Diamor® are copyrights of the Fraunhofer Gesellschaft e.V



amorphous ta-C structure sp³ (C-C) dominated

By courtesy of Dr. HaJo Scheibe Fraunhofer IWS, Dresden

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Hard a-C and ta-C films by novel hybrid PVD processes



Metaplas MZR 304/RF system at IAM

modular PVD/PA-CVD system

reactive d.c./r.f. magnetron sputtering



Hard a-C and ta-C films by novel hybrid PVD processes



modular PVD/PA-CVD system

d.c. cathodic arc evaporation



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Hard a-C and ta-C films by novel hybrid PVD processes

Eröffnung "Werkstofftechnik-Labor"





low temperature deposition up to 500°C large variation in modification of plasma density

plasma particle energies

substrate current density

growth conditions for hard a-C films

Structure and properties of a-C and ta-C coatings



magnetron sputtering

temperature < 100°C, d.c./r.f. bias gradient



Structure and properties of a-C and ta-C coatings



magnetron sputtering

temperature < 100°C, d.c./r.f. bias gradient



temperature < 100°C, d.c. bias gradient



Industrial applications of DLC films - standardization





DLC: Challenges – growth defects in PVD coatings

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DLC: Challenges – intrinsic stress and adhesion



objective: DLC deposition on metal substrates (i.e AISI 316 L)



DLC: challenges – coating delamination and corrosion



DLC coatings for artificial hip joints

in vitro excellent performance of DLC

DLC as wear resistant, chemically inert and biocompatible functional coating

but !

• in vivo: failure of implant

due to failure of interface layer between implant and functional DLC coating by

- crack formation at interface
- crack propagation through interface
- delamination of DLC coating
- corrosion of implant material



DGM News 2010 C.V.Falub et al., Acta Biomat. 5 (2009) 3086 U.Müller et al., Acta Materialia 59 (2011) 1150 R.Hauert et al., Diam. Rel. Mat. 25 (2012) 34 R.Hauert et al., Acta Biomat. 8 (2012) 3170

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DLC: challenges – surfaces with predictable cell adhesion ?



adhesion of thrombocytes on magnetron-sputtered a-C:X coatings





thrombocyte adhesion = f (surface energy, a-C:X constitution, morphology)

DLC: challenges – surfaces with predictable cell adhesion ?



adhesion of thrombocytes on magnetron-sputtered a-C:X coatings



pulsed processes (HIPIMS) hybrid processes high rate deposition

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optimized DLC deposition processes



plasma chemical modification a-C:O:X

surface functionalization

DLC advanced surface topography

nanoscale surface re-arrangement

surface micropatterning

protein interaction at DLC surfaces

Acknowledgement



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A.Welle and team at IBG-1

All colleagues quoted in the presentation

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RESERVE

Growth mechanism in DLC films

example: amorphous carbon, a-C





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subplantation model

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DLC films – R&D milestones and state-of-the-art

1953	H.Schmellenmeier DC glow discharge of C_2H_2
1971	S.Aisenberg, R.Chabot ion beam deposition from graphite
1976/77	L.Holland, S.M.Ohja RF glow discharge of C ₄ H ₁₀
1979/80	C.Weissmantel et al. / K.Enke et al. friction and tribology of DLC
1981	F.K.King carbon films for magnetic recording media
1983	H.Dimigen et al. a-C:H:Me coating film family, Me = W, Ti, …
1986	J.Robertson, Adv. Phys. 35 (1986) 317
1990	D.R.McKenzie et al., H.J.Scheibe et al. arc techniques (filtered arc, laser arc)
1994	M.Grischke et al., and other groups a-C:H:X coating family, X = F, Si, O, B, N
1997/98 > 2000	A.Voevodin J.Zabinski et al. multilayers, gradient coatings, nano- composites, "chameleon coatings"



DLC films – R&D milestones and state-of-the-art



1953	H.Schmellenmeier DC glow discharge of C_2H_2		Karlsruhe Insti	tute of Technology
1971	S.Aisenberg, R.Chabot ion beam deposition from grap	hite	Christophe Donnet	
1976/77	L.Holland, S.M.Ohja RF glow discharge of C ₄ H ₁₀		Ali Erdemir Editors	
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1981	F.K.King carbon films for magnetic reco	rding media	Tribology of	
1983	H.Dimigen et al. a-C:H:Me coating film family, N	Ие = W, Ti, …	Carbon Films	
1986	J.Robertson, Adv. Phys. 35 (19	986) 317	_	
1990	D.R.McKenzie et al., H.J.Sche arc techniques (filtered arc, las	ibe et al. ser arc)	Fundamentals and Applications	
1994	M.Grischke et al., and other gr a-C:H:X coating family, X = F,	oups Si, O, B, N	🖄 Springer	
1997/98 > 2000	A.Voevodin J.Zabinski et al. multilayers, gradient coatings, composites, "chameleon coatir	nano- ngs"		
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Fundamental aspects of cathodic arc evaporation





arc discharge: collective electron emission glow discharge: individual electron emission

kinetic energy of particles 20 - 150 eV(magnetron sputtering 5 - 10 eV)

highly or fully ionized arc plasma multiply charged ions (carbon arc plasma: 60 - 100% C⁺)

droplet & macroparticle emission

cathode spot dynamics = f (cohesive energy of cathode material & magnetic field configuration)

Some aspects of physics of cathodic vacuum arc



1 – 10 μm

 $10^{6} - 10^{8} \text{ A/cm}^{2}$

10⁴ - 10⁵ V/cm

4000 – 40000 K

Me⁺, Me²⁺, Me³⁺

10 - 200 eV

0.1 - 10 MPa

10¹³/cm²

 $10^7 - 10^9 \text{ W/cm}^2$

characteristics of cathodic vacuum arc



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DLC films by reactive d.c. magnetron sputtering (C-DLC)





DLC by laser controlled pulsed arc evaporation (Laser-Arc)





system industrially available \longrightarrow exhibition

P.Siemroth, H.J.Scheibe, IEEE Trans. Plas. Sci. 18 (1990) 911 process parameters & characteristics pulsed laser arc plasma source rotating graphite cathode high vacuum process (10⁻⁴ Pa)

variation of pulsed arc current variation of arc puls duration variation of deposition temperature variation of carbon incident angle

variation of carbon incident angle on the substrate

highly ionized carbon plasma high carbon ion energies (> 30 eV) low substrate temperature (T < 100°C)

coating type 2.2 (ta-C), VDI 2840

VDI 2840 – classification of carbon coatings



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Tabelle 1. Einteilung der Kohlenstoffschichten, siehe auch Erläuterungen im Textteil

		Kohlenstoffschichten												
Bezeichnung (englischer	1 Plasma- polymer-	2 Amorphe K (amorphous	ohlenstoffschi s carbon films,	chten , diamond-like-	-carbon films/[DLC)	3 Kristalline Kohlenstoff-Schichten (crystalline carbon films)							
reality	(plasma- polymer films)									Diamantschichten (diamond films)				
Dünnschicht/ Dickschicht	Dünnschicht				Dünnschicht		Dünnschicht Dickschicht (freitragend)					Dünnschicht		
Dotierung,			wasserstofffrei			wassers	toffhaltig		unde	otiert	dotiert	undotiert	dotiert	undotiert
Zusatzstoffe				modifiziert	modifiziert									
				mit Metali		mit Metall n								
Kristallgröße auf der Wachstums- seite		(amorph)							1 µm bis 500 nm, nanokristallin	0,5 µm bis 10 µm, mikro- kristallin	0,1 µm bis 5 µm	(5 µm bis) 80 µm bis 500 µm	80 µm bis 500 µm	
Überwie- gende C-C- Bindungsart	sp² oder sp³, lineare Bin- dung	sp ²	sp³	sp²	sp² oder sp³	sp³	sp²	sp²	sp ^a	sp ³	sp ³	sp ³	sp ³	sp²
Schicht-Nr.	1	2.1	2.2	2.3	2.4	2.5	2.6	2.7	3.1	3.2	3.3	3.4	3.5	3.6
Bezeichnung	Plasmapoly- merschicht	Wasserstoff- freie amor- phe Kohlen- stoffschicht	Tetraedri- sche was- serstofffreie amorphe Kohlenstoff- schicht	Metallhal- tige wasser- stofffreie amorphe Kohlenstoff- schicht	Wasserstoff- haltige amorphe Kohlenstoff- schicht	Tetraedri- sche was- serstoffhalti ge amorphe Kohlenstoff- schicht	Metallhal- tige wasser- stoffhaltige amorphe Kohlenstoff- schicht	Modifizierte wasserstoff- haltige amorphe Kohlenstoff- schicht	Nanokristal- line CVD- Diamant- schicht	Mikrokristal- line CVD- Diamant- schicht	Dotierte CVD-Dia- mantschicht	CVD-Dia- mant	Dotierter CVD-Dia- mant	Graphit- schicht
Empfohlene Abkürzung	-	a-C	ta-C	a-C:Me (Me = W, Ti)	a-C:H	ta-C:H	a-C:H:Me (Me = W, Ti)	a-C:H:X (X = Si, O, N, F, B)	-	-	-	-	-	-
Weitere ver- breitete, nicht mehr zu ver- wendende Bezeichnun- gen		DLC, graphit- artiger Koh- lenstoff	DLC, i-C, Dia- mant, amor- pher Diamant	Me-DLC, DLC	DLC, a-DLC, Hartkohlen- stoff	DLC	DLC, Me- DLC, Me- C:H, MeC:H, Metal-Carbon	DLC	PCD, PD, NCD	PCD, PD	PCD, PD	Diamantkera- mik, TFD	Diamant- keramik	
Englischer Name	plasma-poly- mer film	hydrogenfree amorphous carbon film	tetrahedral hydrogen free amorphous carbon film	metal con- taining hydro- gen free amorphous carbon film	hydrogen- ated amor- phous carbon film	tetrahedral hydrogen- ated amor- phous carbon film	metal con- taining hydro- genated amorphous carbon film	modified hydrogen- ated amor- phous carbon film	nanocrystal- line CVD dia- mond film	microcrystal- line CVD dia- mond film	doped CVD diamond film	CVD dia- mond	doped CVD diamond	graphite film
Abscheide- verfahren	PA-CVD	PVD	PVD	PVD	PVD, PA-CVD	PVD, PA-CVD	PVD + PA- CVD, PA- CVD	PVD + PA- CVD, PA- CVD	aktivierte CVD	aktivierte CVD	aktivierte CVD	aktivierte CVD	aktivierte CVD	CVD, PVD

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VDI 2840 – classification of carbon coatings



VDI 2840

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	Carbon films													
Designation	1 Plasma	2 Amorphous carbon films 3 Crystalline carbon films												
	polymer films	(diamond-li	ike carbon film	s/DLC)			Diamond films					Graphite films		
Thin film/ thick film	Thin film				Thin film		Thin film Thick film (freestary				reestanding)	Thin film		
Doping,			hydrogen-free			hydrog	enated		und	oped	doped	undoped	doped	undoped
Additional elements				modified with metal	modif with metal			ified with non- metal						
Crystal size on the growth side			(amorphous)							0,5 µm to 10 µm, micro- crystalline	0,1 μm to 5 μm	(5 μm to) 80 μm to 500 μm	80 μm to 500 μm	
Predominat- ing C-C bond type	sp² or sp³, lin- ear bond	sp ²	sp³	sp²	sp ² or sp ³	sp³	sp²	sp²	sp³	sp³	sp³	sp³	sp³	sp²
Film no.	1	2.1	2.2	2.3	2.4	2.5	2.6	2.7	3.1	3.2	3.3	3.4	3.5	3.6
Designation	Plasma poly- mer film	Hydrogen- free amor- phous car- bon film	Tetrahedral hydrogen- free amor- phous car- bon film	Metal-con- taining hydrogen- free amor- phous car- bon film	Hydrogen- ated amor- phous carbon film	Tetrahedral hydrogen- ated amor- phous carbon film	Metal-con- taining hydrogen- ated amor- phous carbon film	Modified hydrogen- ated amor- phous carbon film	Nanocrystal- line CVD dia- mond film	Microcrys- talline CVD diamond film	Doped CVD diamond film	CVD dia- mond	Doped CVD diamond	Graphite filr
Recom- mended abbreviation	-	a-C	ta-C	a-C:Me (Me = W, Ti)	a-C:H	ta-C:H	a-C:H:Me (Me = W, Ti)	a-C:H:X (X = Si, O, N, F, B)	-	-	-	-	-	-
Other desig- nations com- monly encountered but which should no longer be used		DLC, graph- ite-like car- bon	DLC, i-C, dia- mond, amor- phous diamond	Me-DLC, DLC	DLC, a-DLC, hard carbon	DLC	DLC, Me- DLC, Me- C:H, MeC:H, metal-carbon	DLC	PCD, PD, NCD	PCD, PD	PCD, PD	Diamond ceramic, TFD	Diamond ceramic	
Deposition methods	PA-CVD	PVD	PVD	PVD	PVD, PA-CVD	PVD, PA-CVD	PVD + PA- CVD, PA- CVD	PVD + PA- CVD, PA- CVD	Activated CVD	Activated CVD	Activated CVD	Activated CVD	Activated CVD	CVD, PVD

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FZK project MEDICOAT – cell adhesion testing



Bestimmung der Thrombozytenadäsion

Messung nach Methode von Breddin und Brück

- Bereitstellung von frischem Citratblut (Eigenblut)
- zentrifugieren, bis sich PRP (platelet rich plasma) absetzt
- auf in Citratpuffer vorinkubierte Proben aufbringen
- 1h im Brutschrank bei 37° C auslagern
- Proben waschen
- Thrombozyten mit Fluoreszenzfarbstoff (Rhodamin 6G) einfärben
- Auszählung der Thrombozyten im Mikroskop

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MEDICOAT – thrombocytes adhesion on a-C:X coatings



a-C coating with low thrombogenicity



a-C coating with high thrombogenicity



1550 – 1560 cm⁻¹ 34 – 40 mN/m 5 – 9 mN/m 65° - 77°

Raman spectroscopy: G-band position surface energy polar fraction of SE wetting angle of H₂O_{dest} 1565 – 1580 cm⁻¹ 30 – 34 mN/m 9 – 15 mN/m 78° - 90°

thrombocyte adhesion = f (surface energy, a-C constitution, morphology)

MEDICOAT – thrombocytes adhesion on a-C:X coatings



