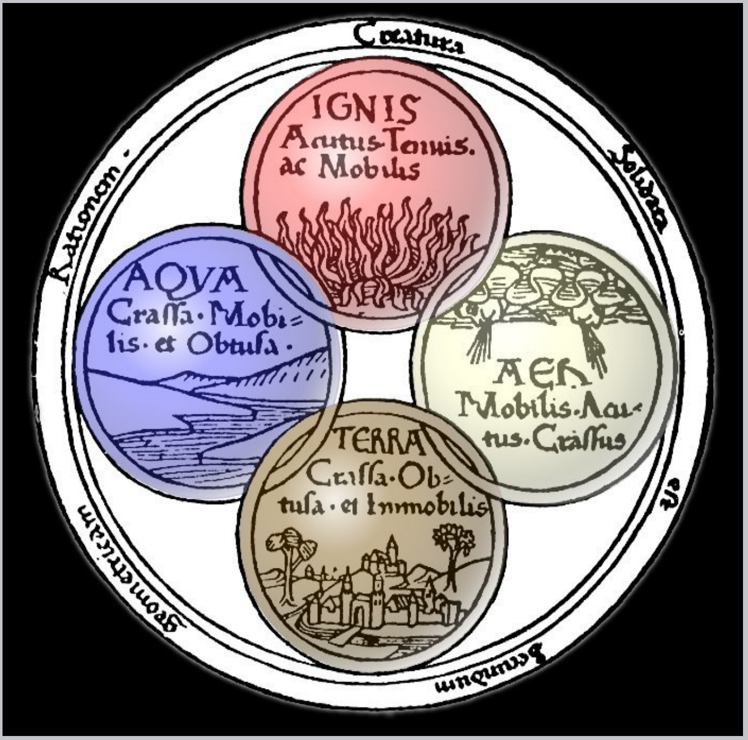
Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating



Tony Anson
(proton@brunel.ac.uk)

www.hvm-uk.com

HVM Graphene+ 2014 Conference –Oxford, UK 15 May

Experimental Techniques Centre

Brunel UNIVERSITY LONDON

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

The application of coatings applied to the surface/s of medical devices (Prosthetics, Instruments, Implants)

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

- Definitions - Coatings
- Coating Types
- Coating Methods
- Physical Properties
- Applications & Commercialisation

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Metals, polymers and ceramics used for medical implants or for externally sited devices, can be coated with other materials to enhance or augment their performance.

This can be used to protect biological tissue from potentially toxic materials that diffuse from an implant, e.g. nickel, chromium, cobalt, in the presence of electrolytes

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Most metals, polymers and ceramics can be deposited onto suitable substrates and there are numerous methods to deposit materials

Polysaccharide coated drugs
Water soluble coating uses
dipping process and drying

DLC coating applied on
the inside of soft drinks
container (diffusion barrier)
To reduce loss of Co2

Pulsed laser deposition of hydroxyl
-apatite on hip prostheses to
improve integration

Catheter, dip coated with
Parylene™ polymer for low friction

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Coating Definitions

Materials can be melted to form a vapour, the vapour is directed onto a cooler surface by condensation or attracted to a surface by applying a magnetic or electrical charge of opposite poles or field, e.g. + to – or N to S. Other processes using a material dissolved in a solvent, can be air sprayed or dipped into solution

Plasma Spraying

Plasma Coating System (CVD)

Optical coatings (PECVD)

Aerosol coating solvent+paint

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Coating Types and Applications

Spraying –	aerosols, solvent vapours
Thermal Evaporation	metal vapour condensation
Dipping –	solvent evaporation
Laser heat-	vaporize coating material
Electron Beam-	heat source to vaporize
Physical Vapour Deposition-	condensation of a vapour onto a surface
Chemical Vapour deposition-	chemical vapours generated by heat react/bond with a target surface

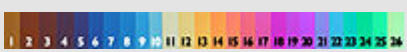
Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

The deposition of thin-films, from a few nanometres to several microns can be categorised by:

1. **Chemical deposition.**

Plating using a material dissolved in a solvent, or electroplating. Gold, silver rhodium, nickel, chromium, tin, copper are common plating materials. Anodising to enhance native oxide films on aluminium and titanium, uses cathode/anode technique

Composite, metal matrix plating using ceramic colloids: Tungsten Carbide, Silicon carbide, Chromium carbide



Colours range available
For titanium anodizing

Aluminium sports equipment anodized for corrosion protection, aesthetics and wear resistance

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Deposition of carbon thin-films, from a few nanometres to several microns can be facilitated by:

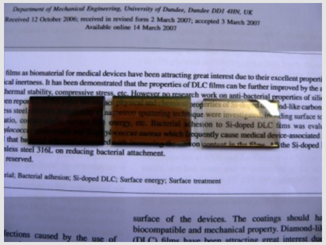
Chemical deposition processes:
Chemical vapour deposition (CVD), Physical Vapour Deposition (PVD) or Plasma Enhanced Chemical Vapour Deposition (PECVD)

A gas/vapour phase of material can be generated by a thermal source, that can consist o
electron beam, laser , electric arc or by forming a plasma at RF (13.56mHz) or microwave (
This produces ions that can be attracted to an object by condensation or an electromagnet
Many materials can be deposited using plasma techniques including metals, oxides (ceram
Both the CVD, PVD and PECVD are used for medical implants
For lubricity, abrasion resistance, diffusion barriers and functionalised biological interface

DLC coated sunglasses

PVD coated watch

DLC coated surgical instrument



DLC coated glass
(varying thickness, 50nm -0.25microns)

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

The deposition of thin-films, from a few nanometres to several microns can be categorised by:

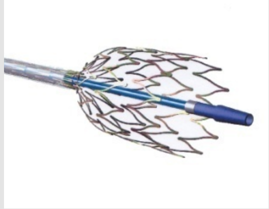
2. Physical Vapour Deposition (PVD)

Evaporative deposition:	**In which the material to be deposited is heated to a high vapor pressure by electrically resistive heating in "low" vacuum. (aluminium coated polyester)**
Electron beam.	**In which the material to be deposited is heated to a high vapor pressure by electron bombardment in a vacuum.**
Sputter deposition:	**In which a glow plasma discharge (usually localized around the "target" by a magnet) bombards the material sputtering some away as a vapor.**
Cathodic Arc Deposition:	**In which a high power arc directed at the target material, vaporizing sacrificial material onto an object**
Pulsed laser deposition:	**High power laser ablates material from the target into a vapor.**

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Ilirazov technique for distraction osteogenesis. The external rings of stainless steel are coated with a thin film of titanium nitride as an abrasion resistant film due to the continuous mechanical fixation friction

Aortic heart valve. The hinge less valve element made from cobalt-chromium alloy is coated with pyrolytic carbon as an anti-thrombogenic coating. This form of carbon is hard and resists continuous impact during the open-close cycles

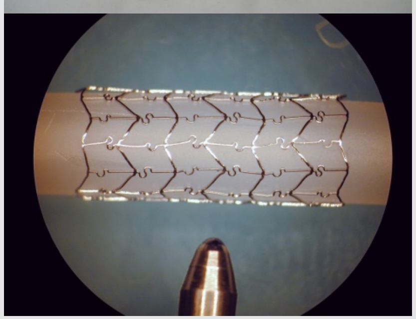


A stainless steel coronary artery stent. Coated with a 20nm film of diamond-like carbon to reduce the potential of nickel or chromium leaching from the device in the presence of body fluids (electrolytes)

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Urinary drainage catheter, made from silicone rubber. One sample is shown coated with diamond-like carbon as a low-friction surface to ease introduction into the bladder via the urethra. The coating also has potential to reduce infection due to the chemical neutrality of carbon

Total knee prostheses made from titanium-aluminium-vanadium alloy. The device is shown with a 1.5micron coating of diamond-like carbon to prevent the diffusion of metal ions from the implant to surrounding tissue



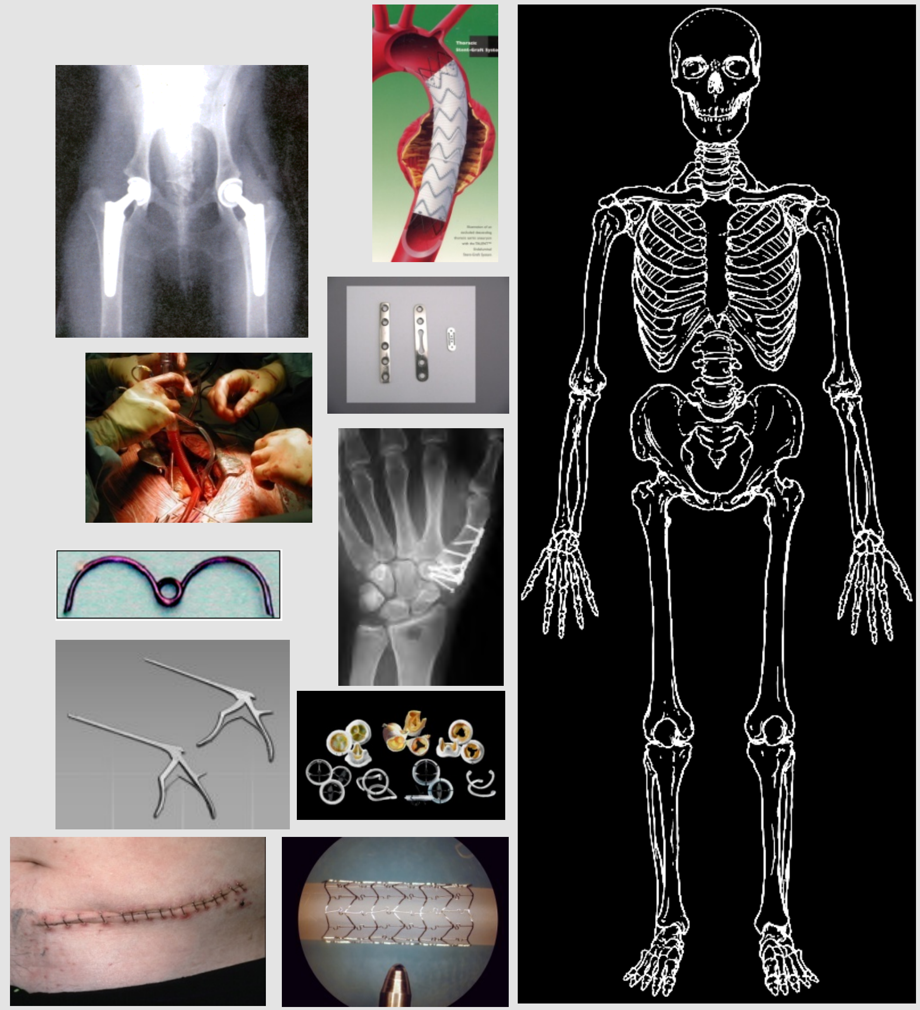
A coronary artery stent from stainless steel. This is a drug-eluting stent with a thin polymer film attached to the stent, containing an immune-suppressant drug to address the problem of restenosis

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Implants & Instruments:

Improving the performance of biomaterials by surface modification (coatings).

- **Reducing migration of metal ions or other undesirable species from implanted device to surrounding hard-soft tissue**
- **Improving introductory techniques**
- **Functionalising surfaces**
- **Integrating biocides (infection control)**



Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Improvements in Biomaterial Performance

The range of materials available to construct medical implant and Instruments is limited and these biomaterials often elicit an immune system response as they are (chemically and physically) foreign objects in the biological system

Medical implants are a known vector that can introduce infection

Metal implants contain bulk or trace elements that are antagonistic for the sensitized patient.

Typically: nickel, chromium, cobalt, vanadium, but many organic constituent, parts of polymers are toxic

Approximately 8% females, 4% males have a nickel allergy

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Case Studies – Thin Film Coatings for Medical Devices

- Biomaterials
- Metal – Polymers
- Coating Types
- Diffusion Barriers + Applications
- Functionalised Surfaces
- Biocides
- Dual Coatings
- Coated Surgical Instruments

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Medical Devices Coatings

Commonly Used Polymer Biomaterials

Polymer	Toxic Precursor chemistry
Polyethylene	**Diazomethane.**
Polytetrafluoroethylene (PTFE-Teflon)	**Fluorine's**
Polyethylene teraphathalate (PET –Dacron)	**Ethylene glycol, xylene**
Polyvinyl chloride (PVC)	**Dioxins, phthalates**
Polyvinyl fluoride (PVF)	**Fluorine's**
Polymethyl methacrylate (Plexiglass)	**Methacrylates**
Poly (2-hydroxyethyl methacrylate) (Hydrogel)	**PVA/Acrylates**
Polysulphone	**Dihydrobenzene/bisphenol**
Polyamide (Nylons)	**Hexamethylene diamine**
Polyurethane	**Di-isocyanate**
Polysiloxane	**Silanes**

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Medical Devices Coatings

Commonly Used Metal Biomaterials

Ti/Al/V	Titanium Aluminium Vanadium (orthopaedic/cardiovascular/general surgery)
Co/Cr/Mo	Cobalt –Chromium –Molybdenum (orthopaedic)
Fe/Cr/Ni	Steel – Chromium – Nickel (general surgery, orthopaedic, instruments)
Pl	Platinum (cardiovascular)
Au	Gold (device coating, radio opaque markers)
Tantalum	Ta (radio opaque markers)
Ni/Ti	Nickel – Titanium (cardiovascular, orthopaedic, general surgery)

- **Potentially toxic, can illicit allergic response**
- **Thrombogenic**

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Medical Devices Coatings

Coating Types and Materials on Biomaterials Using:

Plasma	**diamond, diamond-like carbon, TiN, TiC, HA, polymers**
Ion beam	**carbons, oxides, carbides, HA**
Sputtering	**metals, oxides, carbons**
Thermal spraying (plasma, arc)	**polymers, metals, HA, ceramics**
Electroplating	**metals**
Dipping/Spraying	**polymers, drugs**
Laser deposition	**metals, polymers, HA, oxides**

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Diffusion Barriers

To reduce ion migration in the presence of electrolytes, thin-films of plasma deposited diamond-like carbon has been applied to diverse medical implants.

Diamond-like carbon is a chemically inert film that has low-friction and can resist abrasion. By the addition of fluorine's, nitrogen, oxygen, tissue contact devices can be made hydrophilic *or* hydrophobic demonstrating water contact angles between 60° and 110°

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

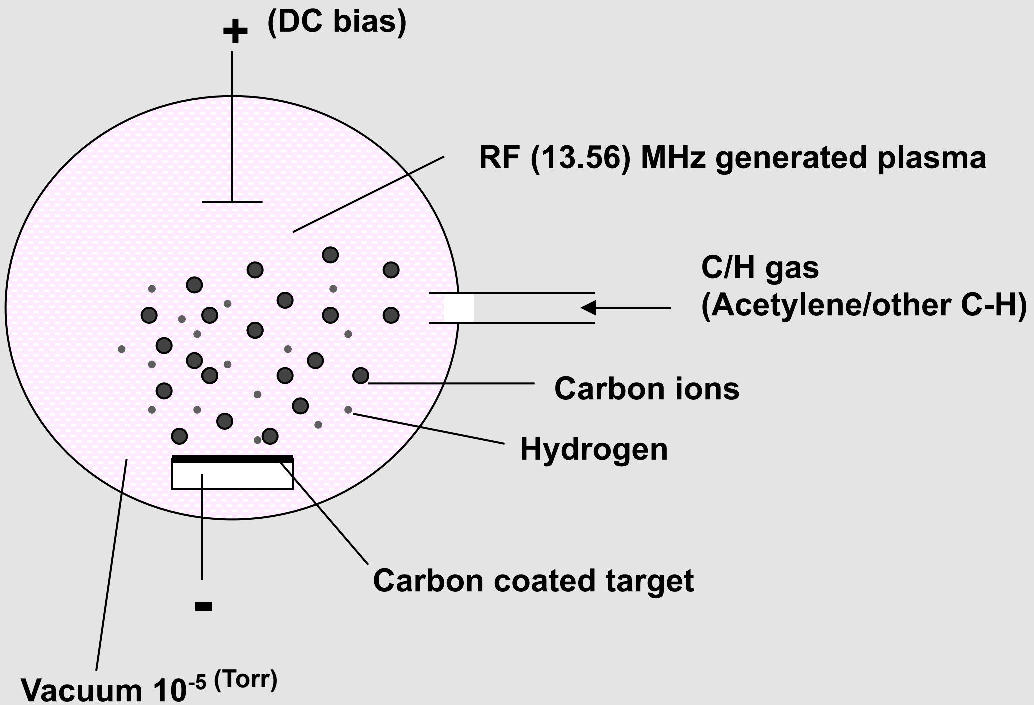
Coating System

PECVD coating system, schematic.

This form of Diamond-Like Carbon (DLC) Is a near-room temperature process with a diffuse plasma extending all to exposed surfaces of the target, (with dark-space-limitation)

The deposited carbon allotrope, DLC is an Sp2/Sp3, (graphite-diamond), <30% H, thin-film, max 4µm.

The 'standard' film has a surface electrical resistance ca. 1200MΩ/cm surface friction 0.08 - 0.1 Mu. and hardness 6-8.5 Moh.



Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Diffusion Barriers

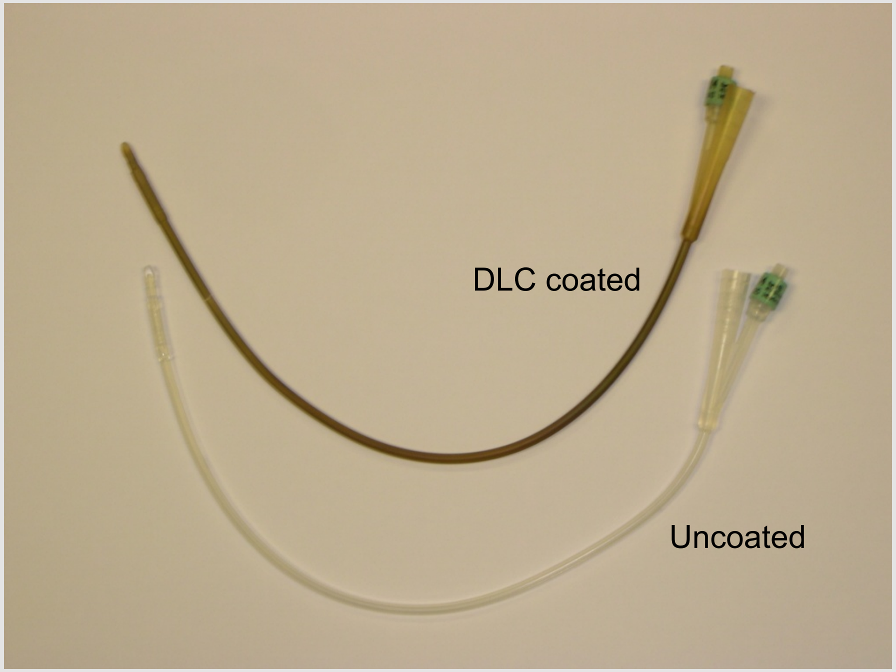
DLC coated total knee prostheses. Double implant used for a patient suffering from broad spectrum metal allergy. Now implanted for 6 years with no evidence of elevated immune system reaction due to the underlying metal structure (ti/al/v)

Uncoated

Coated (ca. 1.5-2.0 µm)

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Diffusion Barriers



Polyurethane urinary catheter

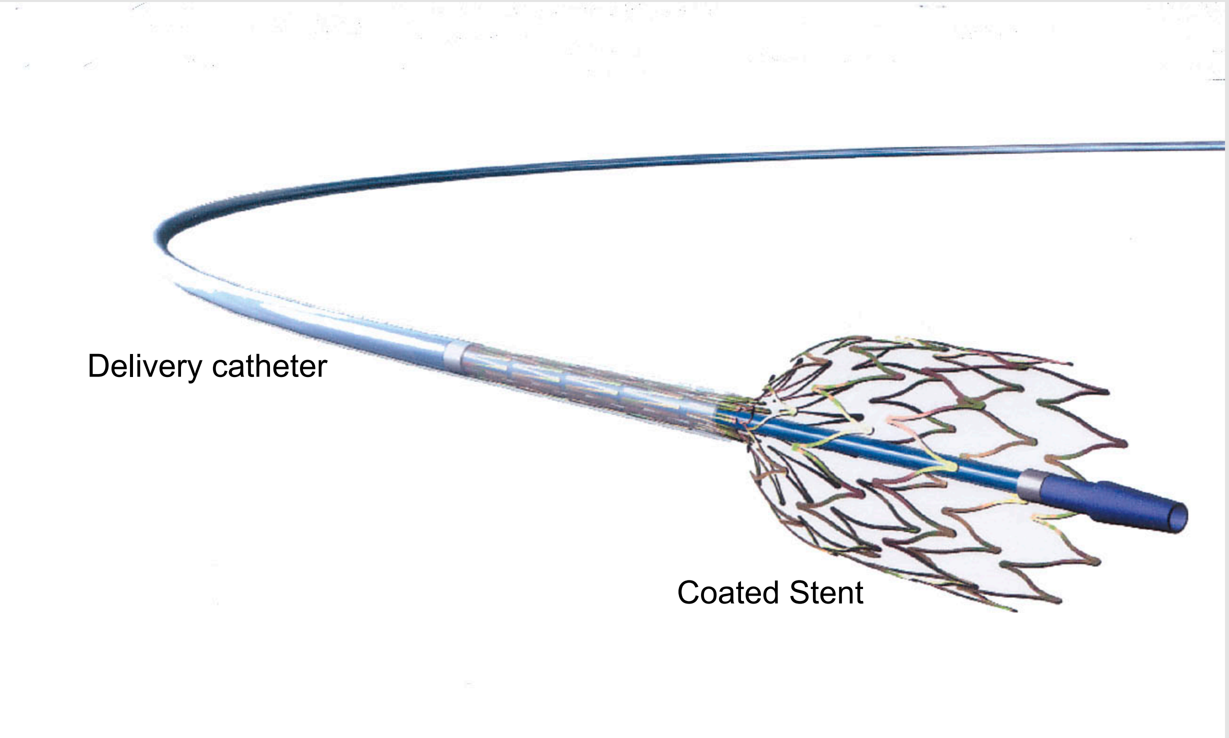
Urinary catheters (short or longer term residency), have two essential problems, bacterial pathway leading to the formation of nitrogenous crystalline compounds forming between catheter-and-tissue.

High friction surface of the catheter can make introduction through the urethra difficult.

DLC is used to reduce infection and to ease introductory trauma due to the low friction properties of the material. Static and dynamic friction is measured as a 'Mu' value: PTFE (Teflon) has a value of 0.04µ, steel, 0.5µ wood,0.3-0.5µ these are approximate figures as temperature, humidity and other physical conditions strongly influence the values shown

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Diffusion Barriers



DLC coated, ni/ti self expanding stent for coronary artery dilation.

The 50nm DLC coating reduces nickel ion migration into the vascular structure.

Heavy metal ion's, resident in the soft tissue is strongly implicated in the progression of arterial restenosis.

Sorin Biomedica Spa. 'Janus' and 'Rainbow' Stent model

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Diffusion Barriers

Histopathology Section of Coronary Artery

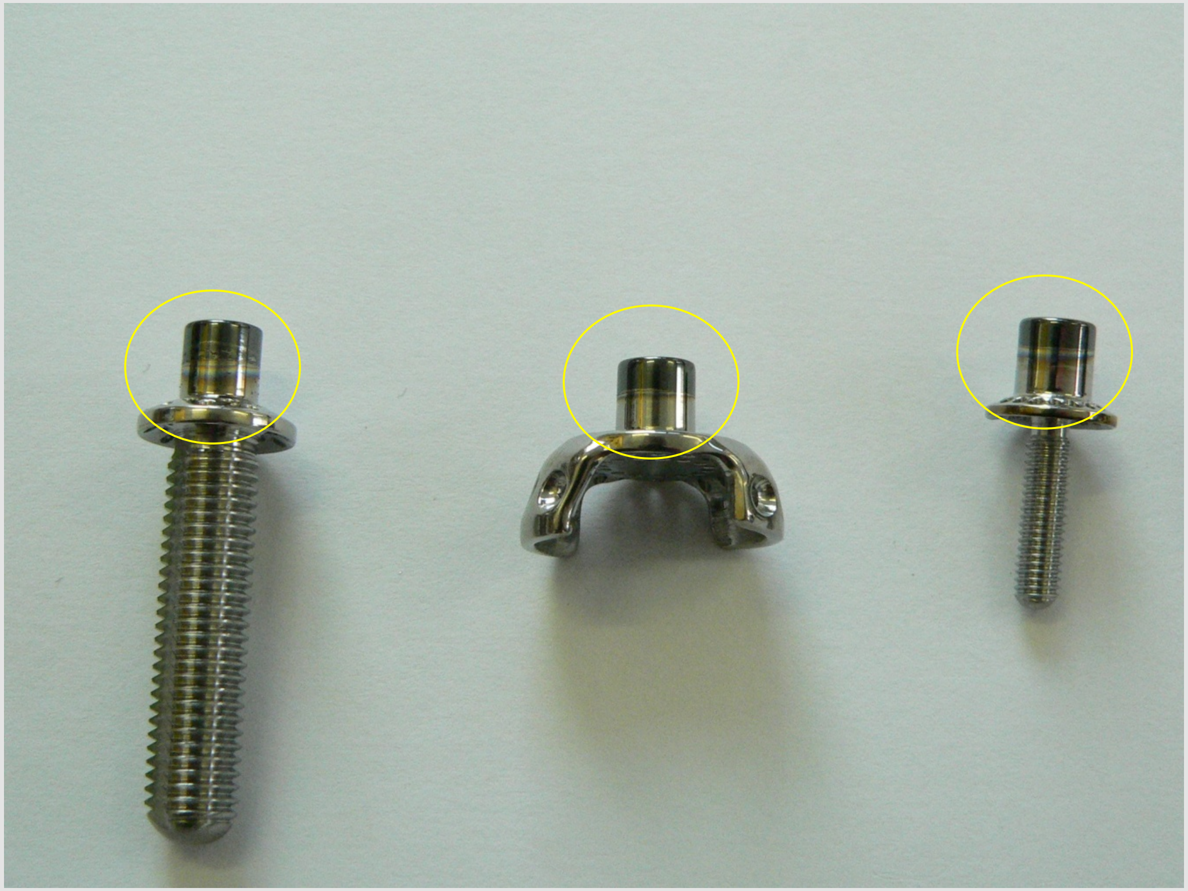
Porcine coronary artery: histopathology Showing restenosis (intimal hyperplasia) - 8 months, post implant.

Indications of nickel ion fibrous encapsulation.

Stent struts

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Diffusion Barriers and Functionalisation

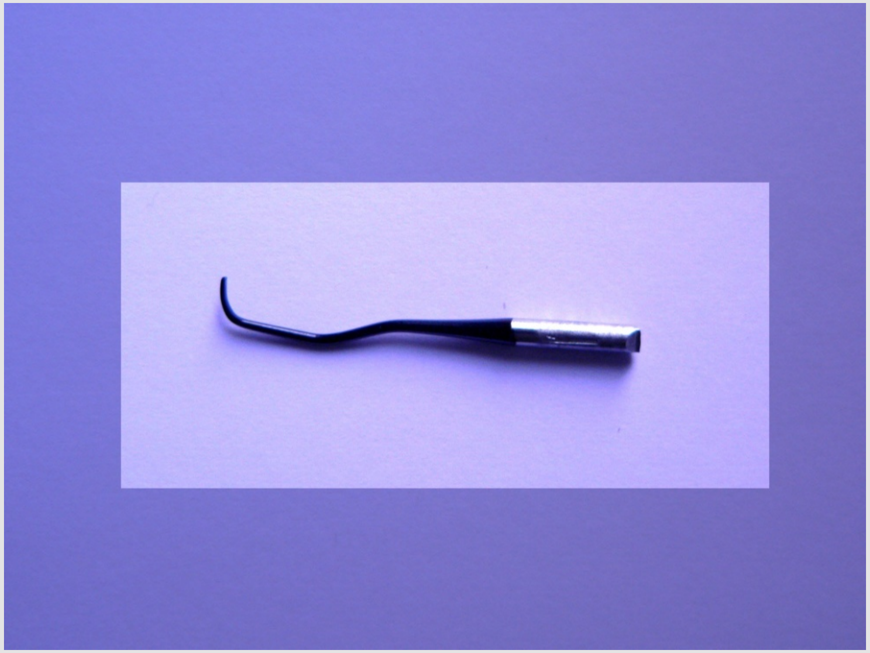


Transcutaneous osteotomy screws for small fracture fixation. The devices present a bacterial pathway leading to potential infection

Zonal DLC coating as a 'natural' diffusion barrier. Surface is conducive to keratin-type cells, Forming a natural barrier, indicating some functionalisation of the DLC surface

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Low Friction Properties



DLC coated dental probe.

The instrument is used to apply adhesives and amalgam, low friction surface prevents adhesive build-up allowing the probe to be used many times.

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Diffusion Barriers and Biocides
Dual Thin-Film Coatings

Hospital acquired infection has increased dramatically in most territories around the globe this may be due to overuse of antibiotic agents (bacterial adaptation) and poor hygiene control in the institutional environment

8% increase in overall Staphylococcus aureus bloodstream infections, from 17,933 (2001/2002) to 19,311 (2003/2004)*.

Denmark 1%	**Netherlands 1%**
Austria 11%	**Germany 19%**
Spain 23%	**France 33%**
Portugal 38%	**Italy 38%**
Greece 44%	**UK 44%**

Reported demographic incidence of hospital acquired infections, Europe 2003-2006

*** UK Department of Health data**

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Diffusion Barriers and Biocides
Dual Thin-Film Coatings

DLC + Ag

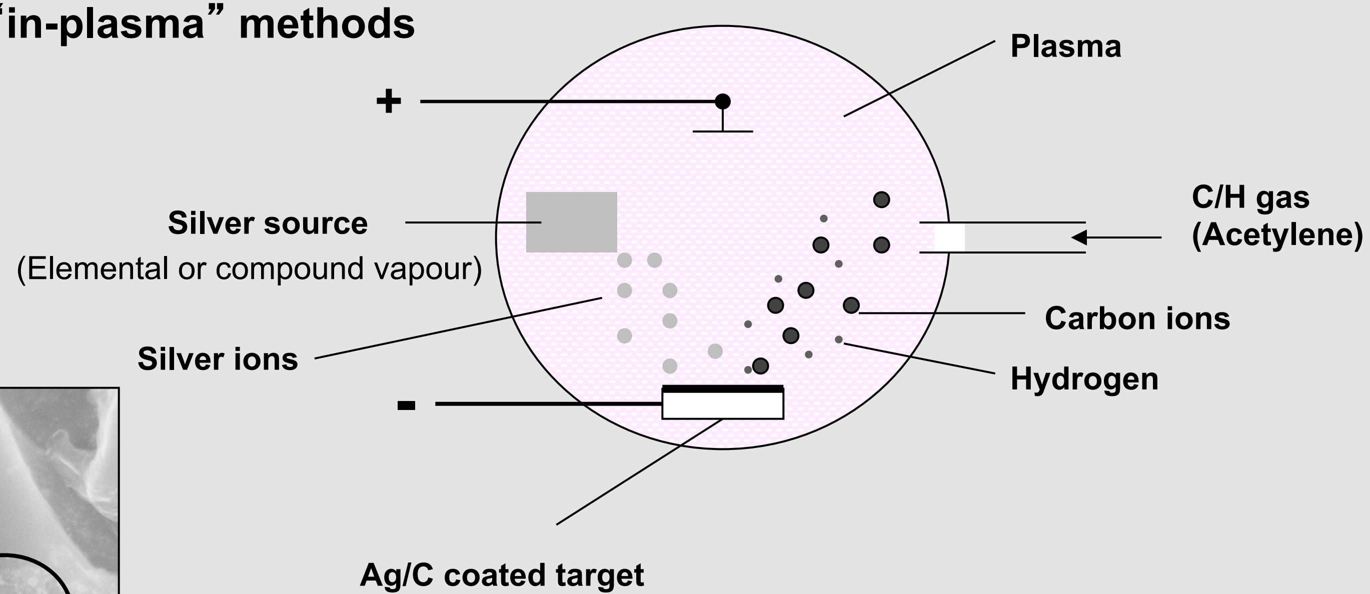
Two methods have been devised and tested to generate diffusion barriers and biocides in a dual arrangement.

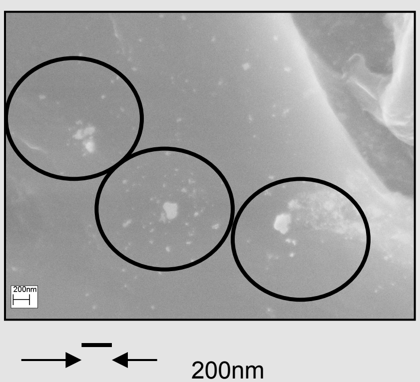
1. **PECVD coating with "in-plasma" –**
 a) saturated AgNo3 solution (silver nitrate)
 b) vaporized elemental silver.

2. **Mask artefact, DLC coat, electroplate after removing mask**

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

1. Direct “in-plasma” methods



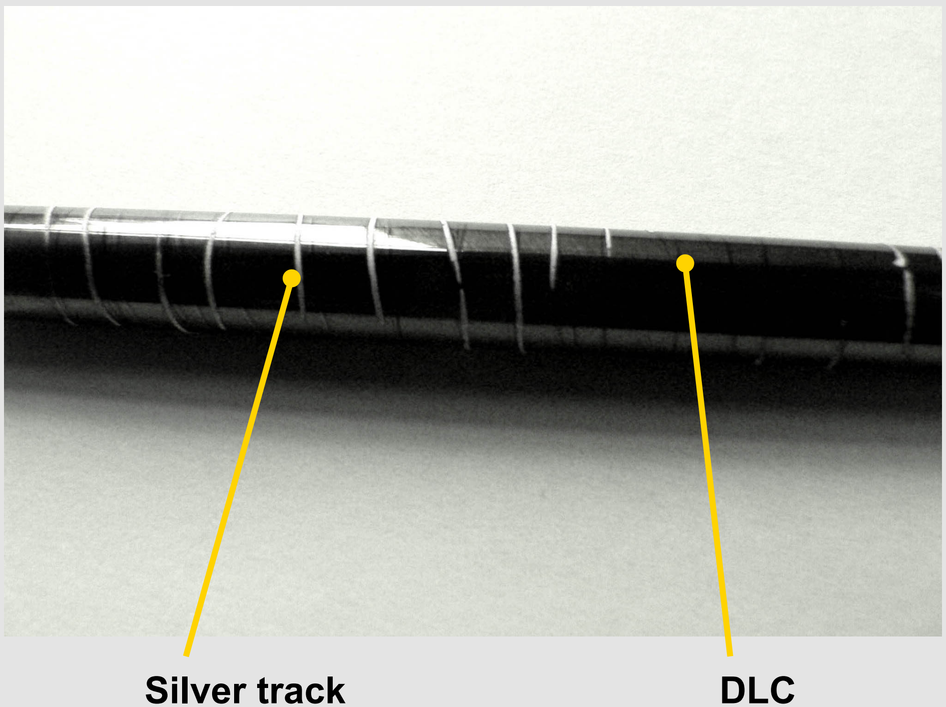


SEM, surface of DLC/Ag
shows clusters of Ag.

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Diffusion Barriers and Biocides
Dual Thin-Film Coatings
DLC + Ag

2. Mask, DLC coat, electroplate.



Test sample stainless steel masked using copper wire formed as a helix around sample, removed after coating and plated with Ag.

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

DLC Used for the Cost Effective Manufacture of Surgical Instruments

DLC coated. HE30TF aluminium structure

Position locking screw

DLC coated alloy steel

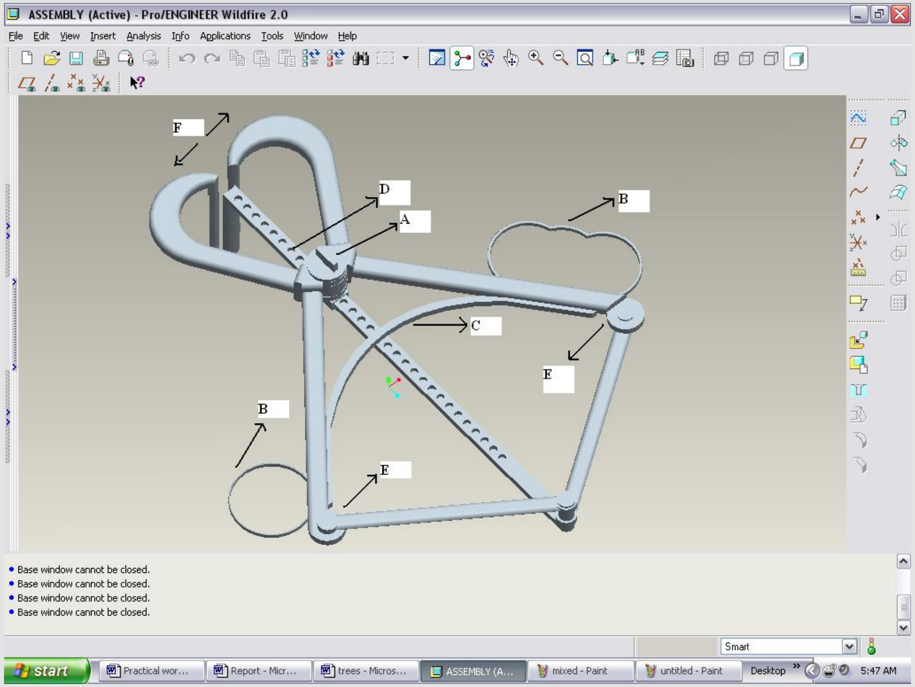
‘Open’ bias spring

Hinge

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

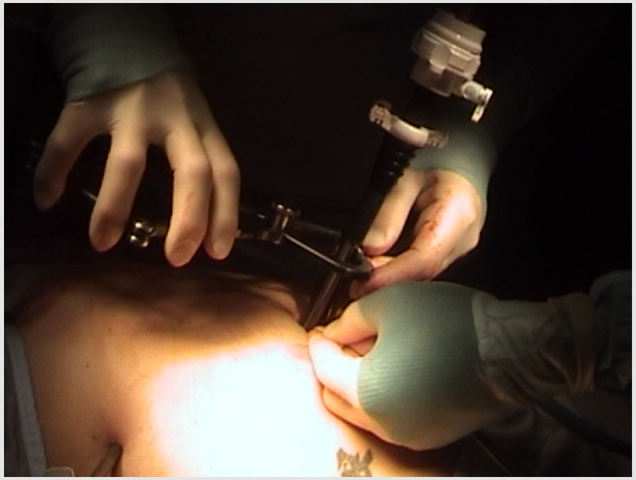
DLC Used for the Cost Effective Manufacture of Surgical Instruments

The instrument is used to dilate small incisons made in the abdominal fascia to effect removal of enlarged gall bladders, without having to increase the size of the incision

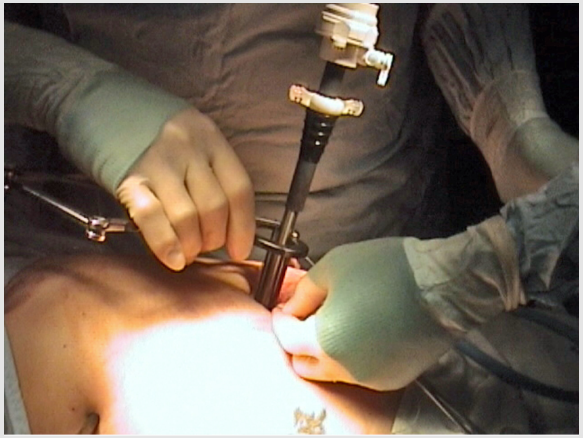


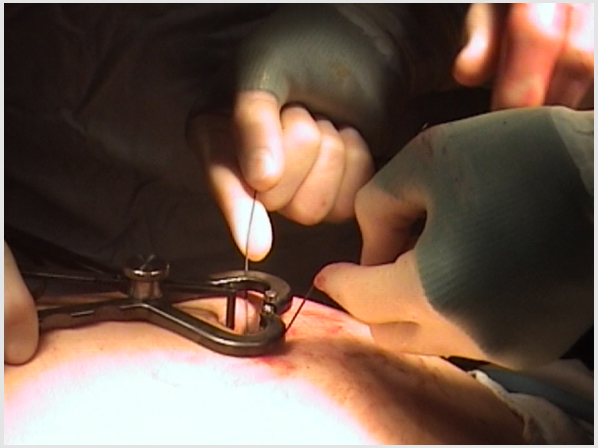
Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

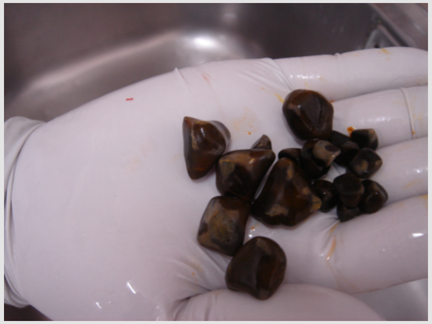
DLC Used for the Cost Effective Manufacture of Surgical Instruments



Instrument in use, in minimally invasive laparoscopic removal of gall bladder







Gall stones to pass through A 1.5cm max. incision ?

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

DLC Used for the Cost Effective Manufacture of Surgical Instruments

Cost effective design conversion of a surgical instruments has been facilitated by the use of easier to machine materials of construction, protected by DLC. [stainless steel manufacture: £1700, aluminium construction £500].

Ergonomic advantage due to light-weight materials.

Low friction thin-films reduce tissue detritus adhesion, to ease cleaning.

Repeated sterilisation (EO, gamma, autoclave, E-beam) does not effect DLC and substrate.

Potential for improved operating theatre, DLC coated disposables, with reduction in incidence of in-hospital infection polymer consumables

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Diamond-Like Carbon appears in several forms and can be produced using CVD, PVD, Ion beam and PECVD: Each type of coating process produces different form of DLC

Property	Dia	a-C	a-C:H	Diamond	Graphite
Crystal Structure	Cubic a_o=3.561Å	Amorphous Mixed sp^2 and sp^3 bonds	Amorphous sp^3/sp^2	Cubic a_o=3.567Å	Hexagonal a=2.47
Form	Faceted crystals	Smooth or rough	Smooth	Faceted crystals	Crystal Planes
Hardness (H_v)	3000-12000	1200-3000	900-3000	7000-10000	
Density (g/cm^3)	2.8-3.5	1.6-2.2	1.2-2.6	3.51	2.26
Refractive Index	-	1.5-3.1	1.6-3.1	2.42	2.15
Electrical Resistivity (Ω/cm)	$>10^{13}$	$>10^{10}$	10^{6}-10^{14}	$>10^{16}$	0.4
Thermal Conductivity (W/m.K)	1100	-	-	2000	3500
Chemical Stability	Inert	Inert	Inert	Inert	Inert
Hydrogen Content (H/C)	-	<30%	0.25-1	-	-
Growth Rate (µm/hr)	~1	2	5	1000 (synthetic)	-

Adding Value to Medical Implants by the use of Diamond-Like Carbon Coating

Conclusion

The use of films deposited onto medical devices, adds to the possibilities in design and functional use. These advantages may be engineering manufacture, longevity, *in-vivo* performance or general service/maintenance.

Some of these attributes have been demonstrated in the examples given, by depositing diamond-like carbon onto a surgical instrument. Other implanted medical devices might also benefit from the relatively biologically neutral surface of these thin-films and the potential for modification to produce selectively conducive surfaces for biological species. The addition of other elements, can address problems of infection and allergic response to substrate materials.

Acknowledgment:
Diameter Ltd
Renishaw Advanced Materials ltd
Wellcome Trust
Stanmore Implants and Royal National Orthopaedic Hospital, Stanmore, Middlesex, UK.
Lombard Medical Technologies Plc. Didcot, Oxfordshire. UK
Hillingdon Hospital Trust, Pield Heath Road, Middlesex UB8 3NN

ETC Experimental Techniques Centre

Brunel UNIVERSITY LONDON