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Medical and Biomedical Thin Film Materials: Prosthetic Implants

Abstract

This is the first in a series of articles addressing medical and biomedical applications for thin films. Applications for these materials are rapidly increasing, with functional organic and biomaterials as one of the most active areas of development. Bio-inspired processes under development include artificial photosynthesis, ferritin regulation, drug delivery, self-healing, self -cleaning, and biological photovoltaics, self-assembled nanostructures and biophotonic materials are also being actively developed. Biological and organic applications include: cancer research, wear resistant and lubricious coatings for implants, antimicrobial materials, oxygenation of blood, drug delivery, antimicrobial treatments, dialysis, gas permeable membranes, self healing, self cleaning and bio-sensors.

Hard, low friction and corrosion resistant thin film coatings are used in a number of biomedical applications, including improving wear and lubricity of implants, wear resistance and lubricity of surgical and dental instruments, coronary and urinary tract stents, and wear resistance of coronary arterial and urinary tract cleaning devices. In addition to resistance to wear and abrasions, adhesion to the prosthesis, biocompatibility, thermal stability and corrosion resistance are important issues that must be addressed. Thin films materials such as diamond like carbon (DLC) and tetrahedral carbon (ta-C), titanium nitride (TiN), titanium aluminu nitride (TiAlN), titanium carbide (TiC), titanium dioxide (TiO_2), chromium nitride (CrN) and alpha alumina (α-Al_2O_3) all show promise. Deposition processes for these materials include magnetron sputtering, plasma assisted CVD (PACVD), plasma enhanced CVD (PECVD), and conventional CVD.

Introduction

Deposition of thin films on solid surfaces can improve a wide variety of properties, including wear resistance, lubricity, corrosion resistance, optical properties, electrical and thermal properties. Thin films can also transform a surface into one with totally new properties, such as decomposition of organic matter and self cleaning windows and surfaces, which makes them also useful for sterilization and chemical remediation [1,2]. One of the most active areas of development in this technology is functional organic and biomaterials. Biological and organic applications include:

- Cancer research
- Antimicrobial materials
- Self-cleaning
- Self-healing
- Sterilization (antimicrobial)
- Oxygenation of blood
- Materials from renewable resources (e.g., algae)
- Bio-sensors

- Drug delivery
- Implants
- Dialysis
- Gas permeable membranes

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The number of hip replacements performed in the United States per year now ranges between 200,000 and 300,000, and is expected to reach 600,000 per year by 2030. The number of knee replacements is outpacing hip replacements and is expected to reach 3.48 million by 2030 [1]. Hip, knee or shoulder replacement, full or partial, is a procedure in which the surgeon removes damaged or diseased parts of the patient's joint and replaces them with new artificial parts. The operation itself is called hip, knee or shoulder arthroplasty. This surgery performed to replace or reconstruct a joint. The artificial joint itself is called a prosthesis and may be made of metal, ceramic, plastic, or various combinations of these materials. Restoration of joint function and mobility is the other major purpose of hip and knee replacement surgeries.

Although the designs for hip and knee prostheses have evolved over the past three decades, and are continually evolving, Figures 1 and 2 show recent designs. Figure 1a shows the components of the prosthesis and Figure 1b shows an x-ray of an implanted hip prosthesis. Hip replacement is a surgical procedure in which the hip joint is replaced by a prosthetic implant. Hip replacement surgery can be performed as a total replacement or a hemi (half) replacement. A total hip replacement (total hip arthroplasty) consists of replacing both the acetabulum (hip socket) and femoral head while hemiarthroplasty generally only replaces the femoral head. Hip replacement is currently the most common orthopedic operation, though patient satisfaction short and long term varies widely.

Femoral heads are made of metal or ceramic material. When they deteriorate the patient experiences a great deal of pain. Metal heads, made of cobalt chromium, austentic stainless steel (e.g., $Fe_{20}Cr_{10}Ni_{2.5}Mo_{0.4}N$), or Co-Cr-Mo alloys [3] for hardness, and are machined to size and then polished to reduce wear of the socket liner. Ceramic heads are smoother than polished metal heads, have a lower coefficient of friction than a cobalt chrome head, and in theory should wear down the socket liner more slowly. As of early 2011, follow up studies in patients have not demonstrated significant reductions in wear rates between the various types of femoral heads on the market. Additionally, ceramic implants must bond to the femur, are more brittle and may break after being implanted. Thus, the motivation to apply hard, wear resistant and low friction thin film coatings or surface treatments to the femoral head to decrease wear rate.

Different combinations of materials that constitute the implant have different physical properties which can be coupled to reduce the amount of wear debris and friction. Typical pairing of materials includes

- metal on polyethylene (MOP)
- metal on crosslinked polyethylene (MOXP)
- ceramic on ceramic (COC)
- ceramic on crosslinked polyethylene (COXP)
- metal on metal (MOM)

Each combination has its own advantages and disadvantages, and each can be improved with the application of wear resistant and low friction thin films and surface treatments.

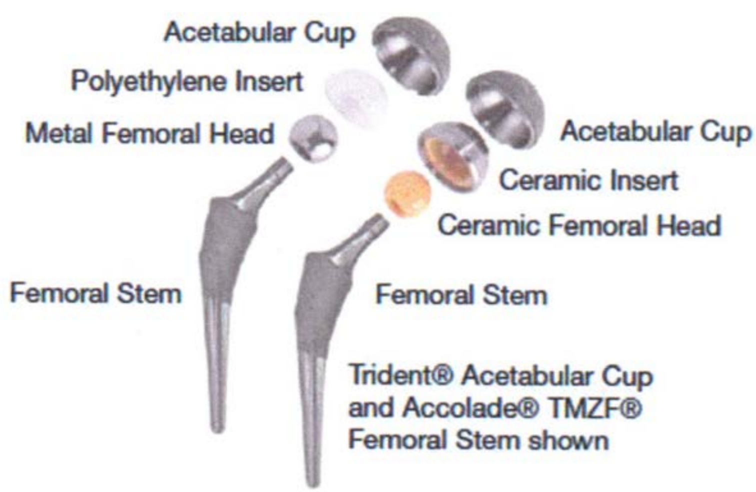

Figure 1a. Hip prosthesis, including acetabular cup, femoral head and femoral stem

Figure 1b. X-ray of an implanted hip prosthesis

This discussion is also applicable to knee and shoulder prosthesis. [Knee replacement] surgery can be performed as a partial or a total knee replacement. In general, the surgery consists of replacing the diseased or damaged joint surfaces of the knee with metal and plastic components shaped to allow continued motion of the knee. Total knee replacement components are shown in Figure 2.

Figure 2. Total knee replacement hardware, including femoral head, tibial plate, patellar plate, and meniscus replacement plate.

Hard Thin Film Coatings for Implants

The main problem with prosthetic joints it that they wear and corrode during extended use. The debris formed as a consequence of wear results in tissue inflammation, osteolysis (active resorption of bone matrix by osteoclasts), and ultimately loosening of the implants. When two material surfaces slide against each other, the softer material is abraded and worn out. The material will also come in contact with human body fluids leading to corrosion of the conjoining surfaces. Thus, for prosthetic joints, the coating material (on each surface) should be hard and inert enough to prevent the wear, corrosion and debris. The coating material should also have good adhesion on the substrate especially in the presence of human body fluid.

Thus we see that there are a number of surfaces in hip, knee and shoulder prostheses that wear against each other, and that reducing friction and wear would significantly improve the lifetime of the implant and reduce failure rate. The implant surface also influences the interaction and adsorption of different proteins, which, in turn, control cell adhesion and behavior [4,5]. As described above, wear between mating surfaces of the prosthesis generates debris that increases wear rate of the surfaces, increases friction and introduces foreign matter into the body (which results in pain). In time the joint can loosen significantly and eventually fail. Reliability issues include

- Biocompatibility: grade 0 nontoxic, non-mutagenic, non-hemolytic, non-progenic
- Improved wear resistance: retention of sharp edges and prevent material erosion in high use areas
- Reduced friction: improved lubricity over uncoated steel, reduced wear and prevention of seizure.
- Improved barrier layer: creates chemically inert barrier, dielectric barrier layer
- Improved corrosion resistance: resists autoclave induced corrosion, improves corrosion resistance of stainless steel
- Aesthetic considerations: identification and distinctive look for market place

Wear resistant and low friction thin film coatings are being developed to mitigate many of the above problems. The body, however, is a hostile environment. For the use of thin film (or that matter, any) materials in the biomedical area some requirements are well defined, while other are not and often not really known [6].

We know that

- Thin film materials must not release any substances, like additives or residual monomers in the case of polymers into the biological environment.
- Thin film materials must not change their properties within the duration of their use. That means they have to be stable against the biological environment. Exception: biodegradable polymers.
- Wear must not accelerate corrosion of the thin film material or underlying component
- Corrosion must not accelerate wear of the thin film material or underlying component

Minimum properties required for wear resistant coatings on implants are:

- High adhesion to the component
- High hardness
- Low coefficient of friction (COF)
- High corrosion resistance to body fluids
- Biocompatibility
- Thermal stability (must survive sterilization)

While a large number of thin film materials excel at one or more of these properties, only a limited number combine all the above properties required for implants [6]. The most promising thin film materials to date for use in the above applications are diamond like carbon (DLC) and tetrahedral carbon (ta-C) [7,8], titanium nitride (TiN), titanium carbide (TiC), titanium dioxide (TiO_2) [8] and alpha alumina (α-Al_2O_3) [9]. Other materials being evaluated are titanium niobium nitride (TiNbN), chromium nitride (CrN), titanium carbon nitride (TiCN), titanium aluminum nitride (TiAlN), silicon carbide (SiC) and zirconium nitride (ZrN) [10]. Note the frequency of transition metal nitrides in this list.

DLC, ta-C, TiN and TiC films have experienced the most development, and are now being marketed [11]. TiN and TiC are two of the first PVD-deposited tribological thin film materials originally developed to replace highly toxic hexavalent chromium (HCr) [12-20]. TiN coatings are being extensively developed for hip, knee and shoulder implants [21]. In addition to implants, TiN is also used in medical devices such as scalpel blades and orthopedic bone saw blades where sharpness and edge retention are important [22]. Useful layer thicknesses range up to ~ 3 µm. TiN is also widely used as a decorative coating, low friction coating and optical heat mirror applications [23,24,24]. Titanium nitride coatings on bearing surfaces of certain hip and knee implants are being marketed in Europe [21], and create a hard bearing surface for articulation with ultra-high molecular weight polyethylene (UHMWPE). TiN coatings exhibit hardness four times greater than that of cobalt chrome alloys (2400HV for TiN compared to 650HV for CoCr) and low surface roughness (R_a<0.05µm). It has enhanced wettability characteristics with synovial fluids and a low coefficient of friction, minimizing polyethylene wear and making it ideal as a bearing surface.

Figure 4 shows a TiN coated knee implant and Figure 5 shows TiN coated hip implants [courtesy Implantcast]. Stoichiometric and highly conductive TiN films have a metallic Au color, while substoichiometric films have a grey-black appearance. This coating also provides protection against third body wear such as polymeric or cement debris. Its scratch resistance prevents implant damage at excessive contact loads. Even with scratch formation, the height of the scratch lip is extremely low, resulting in a substantial reduction in wear as opposed to scratched cobalt chrome implants [26].

Fig. 4 TiN coated knee implant (courtesy Implantcast Fig. 5 TiN coated hip implant (courtesy Implantcast)

TiN ceramic coatings have shown up to 98% reduction in wear against polyethylene in hip simulator studies[27]. Because they are ceramic, TiN coatings have no allergies associated with metal implants, thus protecting patients from adverse allergic reactions. The ceramic layer reduces release of metal ions into the patient's joint space and minimizes bacterial proliferation [28,29]. Particularly for nickel sensitive patients, TiN provides a simple, effective and proven implant solution.

Additionally the mechanical properties of the underlying surface are preserved with TiN coatings, while optimizing the bearing surface performance, resulting in low wear and minimal damage to the component [30,31,32,33,34].

Diamond like carbon (DLC), with its excellent tribological properties, is one of the most promising potential materials to reduce the wear rate and corrosion. The inertness, corrosion and wear resistance, high hardness, low frictional coefficient (COF), and biocompatibility of DLC films have attracted interest for use in orthopedic applications. In addition DLC, the other members of the carbon-based family of thin film materials that have shown promise for use in medical implants includes tetrahedral amorphous carbon (ta-C), amorphous carbon (a-C) and hydrogenated amorphous carbon (a-C:H). There have numerous studies during the last decade to evaluate hard coatings for orthopedic materials to decrease wear rate and biocompatibility for better prosthetic application [35]. To date, in addition to TiN, these thin film materials have the best combination of wear resistance, low COF and biocompatibility. They are being developed for load bearing surfaces of hip and knee implants, and blood contacting implants such as heart valves and stents [11]. DLC, ta-C, a-C and a-C:H are arguably four of the most widely developed and applied thin film materials generally applied to metal surfaces (but also to plastics and glasses) to increase wear resistance and lubricity over the past two decades, and volumes have been published on their properties. Several studies have been performed assessing the wear and corrosion of the biomaterials in artificial joint fluids like bovine serum, saline water, Ringer solution and phospholipids [36,37].

DLC is generally deposited as nanocrystalline diamond. Deposition processes such as plasma enhanced chemical vapor deposition (PECVD), plasma activated chemical vapor deposition (PACVD), microwave plasma chemical vapor deposition (MPCVD), ion beam sputtering (IBS) and filtered cathodic arc deposition (FACD) have the capability to produce DLC, ta-C and a-C:H films. Magnetron sputtering, while providing some energetic particle bombardment, typically produces lower quality films with less sp^3 bonding . Therefore, some form of ion assist is generally required for PVD processes to achieve a high level of sp^3 bonding. Table 2, while not entirely complete, also gives general ranges for deposition parameters and bonding. The Table also reflects the fact that DLC, ta-C, a-C and a-C:H have different applications; hard films may not have lowest coefficient of friction (COF) and alternately, films with low COF may not have highest hardness and wear resistance. Often a compromise must be made to achieve the best possible combination of wear and friction.

DLC is also deposited in microcrystalline, nanocrystalline, and multilayer microstructures. Nanocomposite DLC films are now being developed that have lower wear and friction and significantly higher load carrying capability [7,15].

Progress of DLC, ta-C and a-C:H films for hip and knee Implants

Diamond like carbon

It is still not clear as to the ultimate effectiveness of DLC in improving the lifetime of implants. A number of studies report contradictory results about the effectiveness of DLC coating on the improvement of biomedical performance of materials. These are attributed firstly the wide range of atomic bond structures and materials properties in DLC which depend on the deposition conditions (see above). Care must be taken during interpretation of these contradictory results.

An exact characterization of the DLC coating and determination of its surface properties are necessary to correlate the different in vitro and in vivo results. Secondly, the adhesion of DLC coatings to biomaterials depends on a number of factors, including high residual compressive stress. As a result, the coating can spontaneously delaminate if the adhesion is not adequate, which not only negates wear resistance of the coating, but also degrades biomedical implants by generation of particulates. This problem particularly germane during its use in orthopedic and cardiovascular applications where the medical device faces a number of tensile and compressive stress issues. It has been reported that adhesion is degraded in an aqueous environment mainly due to the interaction between the water molecule and the interface layer.

The risk of spallation, delamination, and corrosion of the DLC coatings during its long-term use in medical implants must be carefully addressed for its use in future biomedical applications. To this end, additional systematic in vitro and in vivo studies are needed to confirm its use in biomedical devices for a commercial basis.

Tribological testing of DLC coated hip joint balls measures sliding wear against UHMWPE (ultra high molecular weight polyethylene) using 1wt% NaCl or distilled water as lubricants [90:10]. As with many tribological tests, results appear to depend critically on test geometry and liquid lubricant used in the test. No significant reduction in the wear of the UHMWPE when sliding against DLC coated femoral heads was reported in all studies using synovial fluid as a lubricant [38]. When bovine serum or synovial fluid was used as a lubricant, different proteins, especially phospholipids, adsorbed on the surfaces, strongly influenced tribological behavior in the joints. Some results, however, may have been skewed by low protein concentrations, showing an abnormal wear morphology. Again, additional testing is needed.

As early as 1993, attempts were made to study the adherence of a-C:H or nitrogen doped a-C films on metal, ceramic, and polymeric joint prosthesis materials by scratch hardness testing [39,40]. Extensive studies were performed assessing wear reduction performance of Co-Cr, alumina, and a-C:H coated Co-Cr with metal adhesion layer against UHMWPE by a special knee wear simulator [41,42]. Figure 6 shows an example of a-C:H coated femoral head of Ti-6Al-4V alloy. The coating was deposited by PECVD. The a-C:H coated femoral head was placed against an UHMWPE acetabular cup. The a-C:H coating was found to successfully suppressed wear of UHMWPE.

Figure 6. Picture of a-C:H coated Ti-6Al-4V alloy femoral head [41].

Table 1 summarizes existing test results for DLC coatings as an orthopedic joint implant [41]. Comparative tests were also made in dry condition to investigate the wear of different materials used in hip joint prostheses against UHMWPE [43]. In a tribological test using the ball-on-disk (BOD) and pin-on-disk (POD) configuration, a-C:H coated stainless steel and titanium have significantly better wear rates than stainless steel, titanium, and alumina and zirconium oxide coated steel alone. A hip simulator was used to study [96:59] mechanical properties of ta-C films deposited by filtered pulsed arc deposition (FACD). Wear rates of ta-C coated metal polyethylene joints are reduced by 10^5–10^6 times compared to metal polyethylene or metal–metal joints. The corrosion rate is also significantly lowered on exposing the coated substrate to a saline solution equivalent to body fluids in 37°C for 2 years. POD tests in simulated body fluid showed that ta-C films applied to both surfaces of UHMWPE and Co-Cr-Mo implants enhanced the lifetime of the implants [44].

Table 1. Summary of test results of DLC, ta-C and a-C:H coatings on orthopedic joint material [41].

	Test Method	Materials	Test	Results on DLC Coating	Reference
Hydrogenated DLC	POD BOD	a-C:H/100Cr6 steel	150,000 cycles in air	Positive; ~10 times decrease in wear rate	64
		Stainless steel (SS), ZrO_2, Alumina, a-C:H/UHMWPE	In dry condition	Positive, but slight decrease in wear rate	58
		SS, ZrO_2, Alumina a-C:H	In bovine serum	Positive; ~100 times decrease in wear rate	65
	Simulator	SS, ZrO_2, a-C:H/UHMWPE	Six million cycles in DW	Positive, but comparable with ZrO_2	61
		SS, CoCrMo, Al, a-C:H	In bovine serum	No significant change	66
		Alumina, Co-Cr-Mo, TiN, N implanted Co-Cr-Mo and UHMWPE, a-C:H	Five million cycles in DW	Positive; ~ 6 times decrease in wear rate	57
Nonhydrogenated DLC	POD BOD	Amorphous diamond (AD) +CoCrMo, AD + SS, AD + Alumina/UHMWPE	50,000–7 million cycles in air, 1% NaCl	Positive; improvement in wear resistance by a factor of 30–600	55
		Uncoated, DLC coated, N ion implanted, thermal oxidation treated, O diffused Ti6Al4V/ UHMWPE	Sliding distance 100 km in water	Negative	63
		DLC + Ti_6Al_4V/UHMWPE	44 km sliding in DW and dry condition	Positive	67
		Co-Cr-Mo, DLC+ Co-Cr-Mo/UHMWPE	Using air, deionized water, SBF	Negative	62
		Co-Cr-Mo, DLC+ Co-Cr-Mo/UHMWPE	Using SBF	Positive	28
		Co-Cr-Mo, ta-C, UHMWPE	Using SBF	Positive; ta-C/ta-C reduces wear ~10^4 times	60
		CrN, TiN, ta-C, a-C:Metal/CrMnNi steel	In DW	Positive	68
	Simulator	Co-Cr-Mo, ta-C, UHMWPE	1300 kg load in saline solution	Positive; ta-C/ ta-C reduces wear 10^5–10^6 times	59
		ta-C/ ta-C	In bovine serum, 15 million walking cycles	Positive; ta-C/ta-C reduces wear10^6 times	69
	In vivo	DLC/UHMWPE, Al_2O_3/UHMWPE	In 202 patients (10 years follow-up)	Negative; survival rate Al_2O_3: 88%, DLC: 54%	37

Abbreviations used: POD, pin-on-disk; BOD, ball-on-disk; DW, distilled water; SBF, simulated body fluid; SS, stainless steel.

In the case of a metal/metal joint with both sides coated with DLC, very low wear rates have been reported for all test geometries and lubricants used, by several research groups [40,41]. The case of DLC sliding against DLC appears to be different than DLC sliding against UHMWPE. Tests performed in aqueous NaCl led to very low wear values, comparable to those obtained in bovine serum, indicating that a similar wear mechanism takes place in both cases. Tests indicated that the buildup of a transfer layer may not be a key requirement for low wear or may not be severely altered by the presence of proteins.

Amorphous hydrogenated carbon (a-C:H) coatings on the stainless steel femoral head were also found to minimize wear against UHMWPE as measured by a hip simulator. Wear of polyethylene acetabular cups against CoCr, alumina, and DLC coated CoCr was measured using a biaxial hip wear simulator using diluted calf serum as the lubricant [45]. *However, note that this low wear obtained using a:C-H coatings was comparable to that of ceramic femoral heads.* Thus, based on tribological tests, the jury is still out on the ultimate benefits of these thin film coatings. Consistent with these results, another study found that DLC coating did not markedly differ from CoCr and alumina in increasing wear resistance against polyethylene [44].

In vivo testing of these coatings also showed mixed results. The clinical failure rate of an eight year follow-up on 101 patients with implanted DLC coated femoral balls (Ti_6Al_4V) articulating against polyethylene showed no sign of problems within the first 1.5 years. However, after 1.5 years, failures began to occur and DLC implants showed aseptic loosening requiring replacement of the implant [46]. After 8.5 years, 45% of the originally implanted DLC coated joints had to be replaced. A large number of mostly round pits were found in DLC coatings on retrieved joint heads. This placed the long term chemical stability of the DLC/Ti_6Al_4V interface in question. Failure was attributed to the stability of the reaction (interdiffusion) layer between the metal femoral ball and the DLC coating, and consisted of a metal carbide or metal hydro oxy carbide. It is well known that there is a synergistic relationship between wear and corrosion [47]. The long-term chemical stability of this reaction layer apparently led to failure under in-vivo conditions, which meant that in addition to the stability of the DLC coating, this interfacial layer must also be biocompatible and survive corrosive wear. Residual stress in the DLC coating and electrochemical processes also exasperated delamination at the interface [47].

Biocompatibility and Thrombus Formation

In in vitro and in vivo studies, a-C:H coatings improved the biocompatibility of orthopedic implants [48]. Amorphous hydrogenated carbon films with sp^3 content in the range 40 to 50% were deposited by acetylene ion beam using a saddle field source. In vitro tests consisted of human fibroblast adhesion and mutagenicity studies, and the in vivo tests were performed by implanting a-C:H-coated stainless steel cylinders in cortical bone and muscular tissue of sheep.

Based on a number of studies on biocompatibility, DLC films shows considerable promise for biomedical applications. DLC coated surfaces demonstrated favorable conditions for the growth of cells like fibroblasts, osteoblasts, and macrophages, without any inflammation and cytotoxicity. DLC coatings in hip and knee joint simulator minimized the wear and corrosion leading to less formation of debris. The release of metal ions from metallic implants was also significantly reduced by DLC. Films were found to

- minimize platelet adhesion and activation,
- prevent thrombogenicity
- improve hemocompatibility in cardiovascular implants.

Doping DLC films with nitrogen also improved biocompatibility .

It is critical that the implant surface prevent thrombus (blood clot) formation. Increased platelet adhesion, activation and aggregation on implant surfaces exposed to blood precede the formation of a thrombus. To this end the first test of any thin film biomaterial is the in-vitro analysis of the hemocompatibility of the coated surface. DLC apparently has the ability to suppress thrombus formation similar or even better than glassy carbon (not to be confused with amorphous carbon: a-C or a-C:H), a material widely used for heart valves. Si-doped DLC coatings have experienced considerable success for stent and guide wire applications [45]. As a result of Si doping, the mechanical, the barrier properties as well as the in vitro bioresponse of DLC coatings have been improved [46]. Only a few papers to date present in-vivo results of DLC coated implants. The hemocompatiiblity of DLC has been shown to be comparable to titanium, cobalt-chromium [49].

DLC-based medical devices are beginning to hit the market; a DLC coated centrifugal ventricular blood pump device (made by Sun Medical Technology Research Corporation, Nagano, JAPAN) coated with DLC was implanted in calves and, even without post-operative anticoagulation, only minor evidence of thrombosis was found on the DLC coated surfaces after explantation. Due to the good hemocompatibility of DLC, a few companies have DLC coated implants already commercially available or in the state of development. The company Sorin Biomedica produces heart valves and stents which are coated by the trade name Carbofilm™. A clinical study on these coated stents, implanted in 122 patients, resulted in a low restenosis rate of 11% after six month [50]. Medicote™ C11 is a DLC coating being marketed by Richter Precision, Inc..

Materion offers solutions to materials and deposition equipment for thin film materials used in prosthetic implants. Sputtering sources for TiN, TiC, DCL and associated alloys are available as well as engineering solutions and the technology to deposit these materials.

Sputtering Targets

Evaporation Materials

Thin Film Deposition Materials

Recommended Reading

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