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DLC coating of textile blood vessels using PLD

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Abstract Textile blood vessels with a length of 30 cm were coated with amorphous diamond-like carbon (DLC) layers with thicknesses up to 200 nm. The layers were created by pulsed laser deposition in vacuum or argon ambient. The percentage of sp^3 carbon was evaluated using X-ray photoelectron spectroscopy, X-ray excited Auger electron spectroscopy and Raman spectroscopy. Depending on the deposition conditions the sp^3 content varied from ∼40% to 60%. The adhesion of the DLC layers to the textile vessels was checked. The preliminary biocompatibility results from in vivo tests with sheep are also given.

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1 Introduction

To replace parts of a human body, various prostheses and materials are applied. The acceptation of the prostheses by the body can be improved by coating of the implants with layer of biocompatible material. In the past decade, carbon has been found to be an excellent candidate as a coating material for medical applications. Carbon has been well established as a material exhibiting good biocompatibility, perhaps due to its unique position as a basic element for all organic systems. Its ability to form bonds in sp, sp^2 and sp^3 configurations is in the basis for the diversity of the carbon materials [1]. Tissues can adhere well to carbon implants and sustain a durable interface. In presence of blood, a protein layer is formed which prevents the formation of blood clots at the carbon surface [2]. Thus, for medical prostheses being in contact with blood (heart valves, anathomic sheets, stents, blood vessels, etc.), diamond-like carbon (DLC) coatings can be used. DLC layers are amorphous or contain micro- or nanocrystalline diamond or graphite as well as a disordered structure with a mixture of bonding configurations. DLC can be hydrogen free (a-C) or containing hydrogen (hydrogenated amorphous carbon (a-C:H)). DLC films exhibit excellent physical and chemical properties, as well as high level of biocompatibility [3]. The films are dense, mechanically hard, smooth, impervious, abrasion resistant, IR transparent, chemically inert, resistant to attack by both acids and bases; they have a low coefficient of friction, low wear rate, and are biocompatible and thromboresistant [4, 5]. DLC coatings can be adherent on a range of biomaterials and no toxicity toward the tested living cells and no inflammatory response or loss of cell integrity were reported [6]. DLC shows an excellent hemocompatibility, a decreased tendency of thrombus formation and coated heart valves and stents are already commercially available [7].

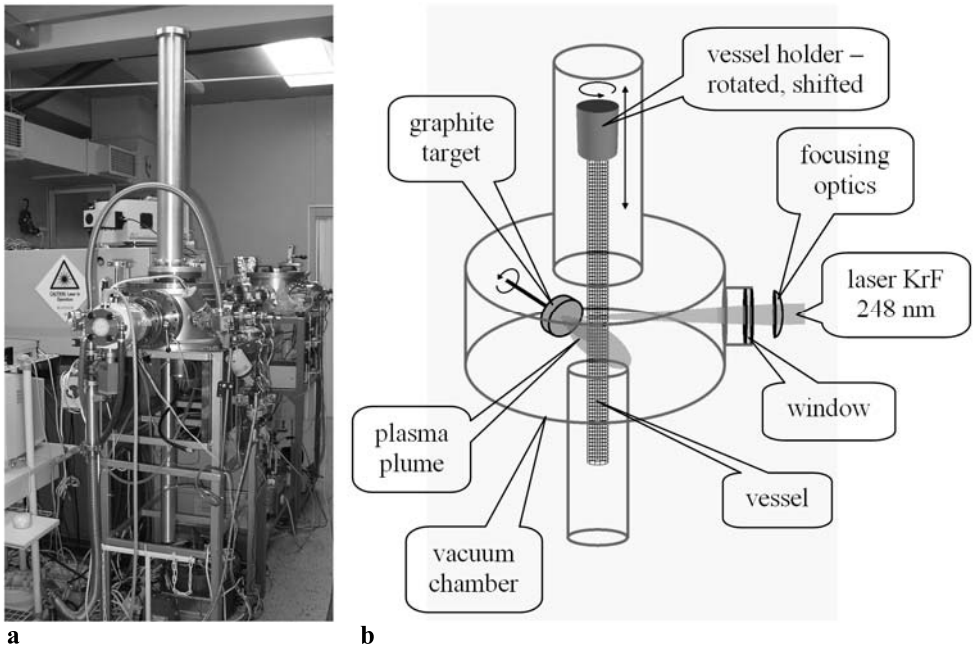

Fig. 1 Deposition system for coating of textile blood vessels: **a** photo of a vertical coating system, **b** scheme of the deposition system

The properties of the DLC coatings depend strongly on the hydrogen content and sp^3/sp^2 ratio which, in turn, depends on the deposition process and its parameters. The range of the properties of the DLC produced by different methods and under different process parameters is considerable.

Artificial blood vessels composed of viable tissue represent the ideal vascular graft. Compliance, lack of thrombogenicity, and resistance to infections as well as the ability to heal, remodel, contract, and secrete normal vessel products are the theoretical advantages of such grafts [8]. Artificial blood vessels are fabricated from polyethylene, polyurethane, textile, etc., the tubes possess inner diameter of several tenths of microns to several millimeters. By coating of the tube less thrombogenic and thus more compatible with living issue surfaces can be prepared.

In this work, we studied the conditions for coating of artificial textile blood vessels with hydrogen-free amorphous DLC layers. The layers were prepared by pulsed laser deposition (PLD). The geometrical configuration of the coating arrangement, the thickness of layers, sp^3-content, and the results from in vivo tests with sheep are presented and discussed.

2 Experimental

Deposition—the films were prepared by PLD using a KrF excimer laser ($\lambda = 248$ nm, $\tau = 20$ ns, $f = 13$ Hz). The carbon species were ablated from a high purity graphite target with an energy density of the laser beam on the target in the range of 10–20 J/cm^2. The layers were deposited in vacuum or in argon ambient (pressure up to 1 Pa). The base vacuum of the coating system was 5×10^{-4} Pa. For the study of the film properties, silicon or fused silica substrates were used; textile blood vessels were coated for in vivo tests. The target-to-substrate distance ($d_{T\text{-}S}$) was kept at 40–50 mm. The DLC layers were created at room substrate temperature which made possible to coat the textile tubes without any destruction of the vessel material.

The goal was to coat textile blood vessel with a diameter of 7 mm and length up to 30 cm. Several deposition arrangements were tested: special rotated planetary system which enabled to cover all tube surfaces, rotatory/rewind system in which the tube was rewound from one spool to another, rotatory/shifting horizontal system and rotatory/shifting vertical system. The last one is relatively simple and makes it possible to cover homogeneously textile tubes of length up to 60 cm (Fig. 1). The laser beam is focused on a graphite target and the textile tube is shifting up and down perpendicularly to the plasma plume. When the tube reaches the upper position (related to the plasma plume) the direction of shifting of the tube is automatically changed and the tube is moving down. At the lower position end, the direction of tube shifting is changed again. The cycles are repeated until the thickness of DLC coating reaches the preselected value. The textile tube is not only shifted but also rotated. As a result, the whole selected length of the tube is homogeneously covered with DLC layer.

For the coating of textile tube length of 30 cm with DLC layer of thickness up to 200 nm, the number of required deposition pulses is in the range of several tens of thousands. The ablated material is collected not only on the substrate but partly also on the laser input window. Thus, for longer

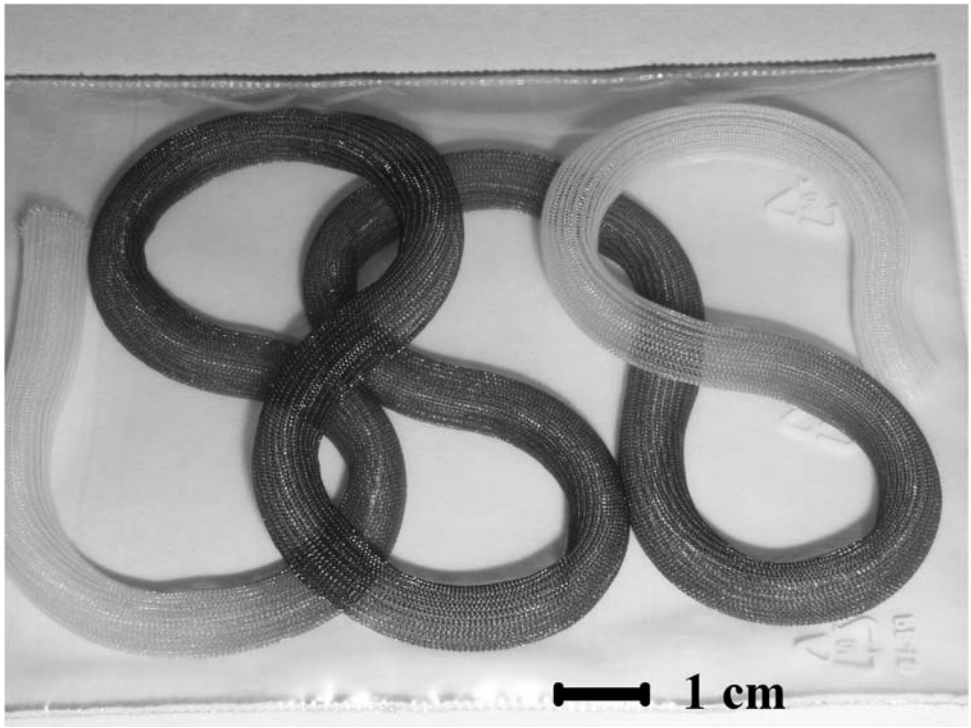

Fig. 2 DLC coated textile blood vessel of 7 mm diameter and 30 cm length (created in 0.25 Pa of argon, 20 J/cm^{-2})

deposition time, the window starts to contaminate and its transmission decreases (the decrease of transmission was about one third for 100 000 deposition pulses). The problem was overcome by using a stream of argon directed on the input window, i.e., the DLC coating was created in argon atmosphere.

Blood vessels—we used textile tubes (type ARTEKOR) with scrim knitting. In such a case, the stream of the depositing carbon material is passing also through the tube and both the inner and the outer surfaces of the tube are covered. An example of DLC coated textile blood vessel is presented in Fig. 2.

Characterization of layer properties—the film thickness was determined by a mechanical profilometer. The chemical bonding of carbon atoms (sp^3- or sp^2-hybridization) in the films was investigated by X-ray photo- and Auger electron spectroscopy (XPS, XAES, ADES-400 VG Scientific) with Al $K\alpha$ radiation and 20 eV pass energy applying C 1*s* and C KLL line shape analyses. The spectra were recorded without sputter cleaning of the analyzed sample surfaces in order to prevent ion-beam induced changes in the surface composition and bonding. It should be noted that air-exposed carbon surfaces were applied also for the in vivo tests. In any case, the surface contamination by oxygen was rather low, around 3 at.%. Both methods were used for estimation of the sp^3/sp^2 ratio, as described below. Importantly, the C KLL Auger electrons result in a very shallow sampling depth of ∼3 nm due to the low electron energy involved (∼270 eV). Contrary, the C 1*s* electrons with ∼1200 eV electron energy possess a sampling depth of about 9 nm [9, 10]. Micro-Raman spectroscopy (Renishaw Ramanscope model 1000, Ar^+ ion laser $\lambda = 514.5$ nm) was used also for study of the bonding nature of the DLC coatings. Their adhesion to the textile vessels was indirectly tested in an ultrasonic bath.

In vivo tests—Eight Merino schaf sheep, 4 to 5 years old, with weight between 55 and 106 kg were used for the experiments.

3 Results and discussion

3.1 Deposition

It is not known which layer thickness is the most suitable for coating of textile vessels. From production point of view, the film thickness should be as small as possible (shorter deposition time, small contamination of the input window with DLC materials, lower production cost, etc.). From medical aspect, the required optimal film thickness is also not known. In any case, the DLC coating has to exhibit excellent hemocompatibility and decreased tendency of thrombus formation. Another open problem concerns the most suitable sp^3-C content (also connected with the production price and with the medical and mechanical properties of the coating). To prevent decreased transmission of the input window, we used argon flow directed to the place of introduction of the laser beam into the chamber. In order to investigate the influence of the argon on sp^3-C content, we created DLC layers on Si and fused silica substrates in vacuum and in different argon ambients (up to 1 Pa).

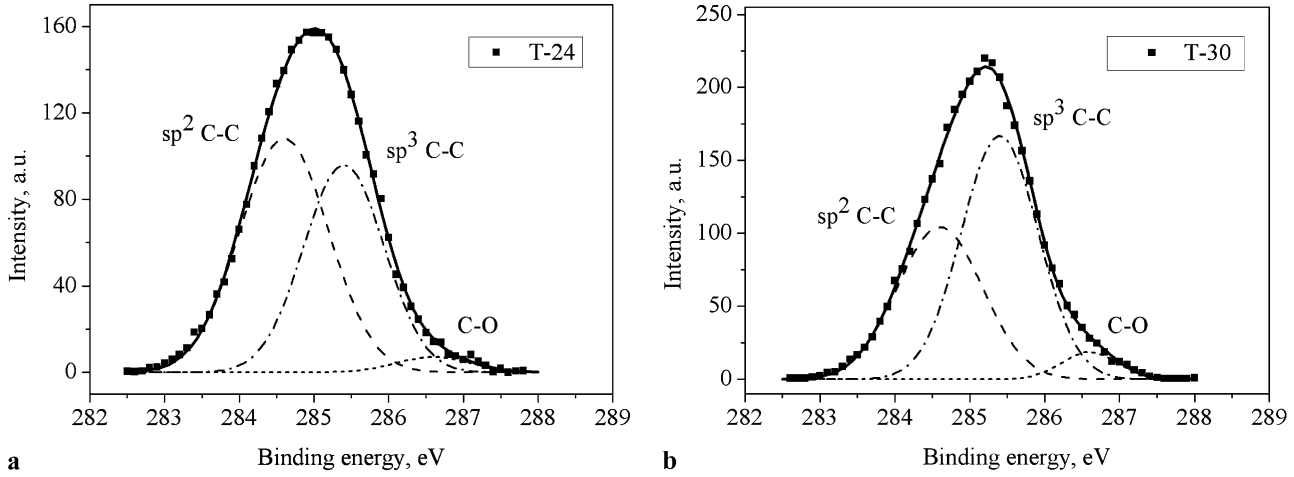

Fig. 3 Deconvoluted C 1*s* X-ray photoelectron spectra of DLC films on silicon substrates created **a** in vacuum (T-30) and **b** in 1 Pa of argon (T-24)

Table 1 Results of the deconvolution of C 1*s* XPS peaks and AES of DLC films prepared by PLD ($d_{T\text{-}S} = 4$ cm, laser energy density 20 J/cm^2) at different ambients and pressures

Sample	Deposition ambient [Pa]	XPS						AES
		FWHM sp^3 peak [eV]	ΔBE1 [eV]	FWHM sp^2 peak [eV]	sp^3 content [%]	ΔBE2 [eV]	Oxygen content [at.%]	sp^3 content [%]
T-24	1.0 Ar	1.07	0.8	1.18	44	1.2	3.0	42
T-25	0.5 Ar	1.00	0.8	1.15	50	1.2	3.8	42
T-29	0.25 Ar	0.99	0.8	1.14	53	1.2	4.6	40
T-30	2×10^{-4}	1.02	0.8	1.13	59	1.2	4.7	55

3.2 Fraction of sp^3-bonded carbon atoms

The content of "diamond" sp^3-C determines the properties of the DLC and gives the information of how much the coating is "diamond"-like. In machinery, there is a requirement to obtain hard DLC coatings, i.e., the goal is to fabricate layers with very high sp^3 content (more than 95%). Such layers are usually very brittle. For medicine, the optimal sp^3/sp^2(diamond/graphite) ratio is not known. There are several examples for applications of DLC coatings in the medicine, but no data about sp^3/sp^2 ratio were published. Probably its optimal value depends on the applications—the coating should be harder for metal prostheses (heart valves, etc.), while for coating of plastic materials (stents) or textile vessels, the layer could be softer and more flexible (i.e., more graphitic). We studied the influence of the ambient (vacuum or argon) on the chemical bonding structure of DLC using XPS, XAES and Raman spectroscopy.

X-ray photoelectron spectroscopy: the measured C 1*s* spectra were deconvoluted as shown in Fig. 3. From the figure, it is evident that three contributions have to be taken into account for the C 1*s* peak. The peak with a higher binding energy from those with similar intensities can be attributed to sp^3 bonded carbon (C–C and C–H). The FWHM of the sp^3 peak was 1.0–1.1 eV for all samples. For the remaining two peaks, the binding energies are given with respect to that of the first peak. The contribution at $\Delta E_1 \approx -0.8$ eV can be identified with sp^2 carbon. It is in a good agreement with predicted C sp^2 and C sp^3 peak separation (1.1 ± 0.2) eV [11]. The FWHM of the sp^2 peak was 1.1–1.2 eV for all DLC films. The content of sp^3 carbon in all films under investigation was evaluated from the corresponding peak area, weighted by the sum of the sp^3 + sp^2 areas; the results are summarized in Table 1. The areas of the peaks were determined following Shirley's inelastic background subtraction mode. A decrease of the sp^3 fraction in the DLC films was observed with the addition of argon and with the increase of its pressure. The third peak at $\Delta E_2 \approx 1.2$ eV can be identified with C–O bonds, which are due to surface contamination after film exposure to the air [12, 13].

X-ray excited Auger electron spectroscopy: it is a fingerprint method based on the observation of different widths of the valence band of graphite and diamond [14]. The difference can be easily elucidated also from the width of the C KLL Auger transitions, described by the so-called *D* parameter [12] because the transition can be considered as a convolution of the valence density of states. Therefore, applying linear interpolation between the *D* values for graphite and diamond, content of sp^3- or sp^2-C in the surface region of a carbon film can be easily calculated. The results are summa-

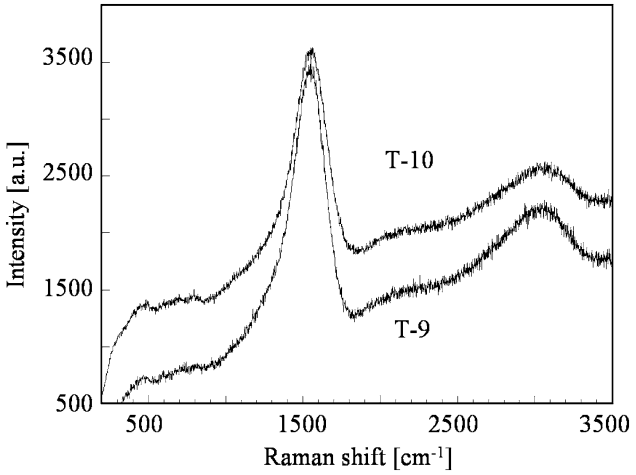

Fig. 4 Micro-Raman spectra of DLC layers on fused silica substrates (20 J/cm^2, vacuum, $d_{T=S} = 5$ cm, T-9—1500 laser shots, T-10—3000 laser shots). Ar^+ ion beam was focused to a spot of 4 mm in diameter

rized in Table 1 and compared to those obtained from the C 1*s* spectral line shape analysis. The values for sp^3-C content derived from the C KLL lines are slightly smaller, ranging from 40–55 %. The difference can be due to the different sampling depths of C 1*s* and C KLL electrons, as mentioned above.

Raman spectroscopy (*RS*): the Raman spectra of DLC layers created on fused silica substrates in vacuum are shown in Fig. 4. The spectra are essentially the same, indicating good reproducibility of the deposition process. An asymmetric band peaking at about 1550 cm^{-1} can be observed in all spectra. Its shape and position point that the samples may be classified as tetrahedral amorphous carbon (ta-C) [15]. The background increasing to higher frequencies is due to the photoluminescence from the substrate and/or the film/substrate interface. Indeed, for the fluence used (20 J/cm^2), the sp^3 content in such PLD films may be as high as 80%, as reported in literature [16]. We fitted the experimental curves to the Breit–Wigner–Fano or skewed Lorentzian lineshape [17]. No additional bands were necessary for the fitting, justifying the classification of the samples as ta-C. The band asymmetry is described by the coupling coefficient Q (the pure Lorentzian shape is recovered as Q^{-1} approaches zero), which is sensitive to the sp^3 content variation [17]. As expected, the Q values in both samples were very similar (-4.2 and -5.3 for samples T-9 and T-10, respectively). It corresponds to sp^3-content between 45 and 55% [17]. According to the absorption spectra presented in [18], the penetration depth at a wavelength of 514.5 nm in ta-C amounts to more than 500 nm. Therefore, we get information across the whole thickness of the sample. It is interesting that our estimation of the sp^3 bond content agrees well with the values determined by the electron spectroscopic methods, which probe the very surface of the material. In fact, both cases when the surface sp^3 content exceeded the bulk value [19] and vice versa [20] were reported in literature.

3.3 Adhesion

The adhesion of the DLC layers to the textile vessels was tested indirectly, using ultrasonic bath. The coated vessels were placed into a bath with physiological serum and shattered in it about 30 min. We checked the change of the vessels morphology with an optical microscope and visually the change of the liquid color. No removal of DLC materials from the vessels was observed.

3.4 In vivo tests with sheep

Comparing the results from the measurements of sp^3 content and of the decrease of input window transmission after various regimes of deposition, we decided to coat the textile vessels in 0.25 Pa of argon atmosphere. In such a case, the decrease of transmission after long time deposition is neglectable and the decrease in sp^3 content is also small. Two sets of vessels with "harder" DLC coatings (higher "diamond" content, energy density of 20 J/cm^2) of various thickness (200 nm and 20 nm) and one set with "softer" coating (more "graphitic", energy density 10 J/cm^2, layer thickness 150 nm) were prepared. The coated and non-coated (used as a reference) prostheses were operated into *arteria carotis* of sheep on both sides. After 100 days of the healing process the sheep were sacrificed. The preliminary results show that no remarkable difference between various types and thicknesses of the DLC coatings was found. More details will be given after the evaluation of the results from immunohistological tests [21].

4 Conclusions

DLC layers were created in vacuum or in argon ambient (up to 1 Pa) using PLD. Argon was used to prevent the decrease of transmission of input window after long time deposition. The sp^3-C content in the DLC layers was studied using XPS, AES and Raman spectroscopy. The layers created in vacuum exhibited 55–59% sp^3-C fraction (AES, XPS), or 45–55% (RS), while those created in 1 Pa of argon exhibited 42–44% sp^3-C. The difference in the results for sp^3-C content can be explained by the different sampling depths and areas. While Raman spectroscopy provides bonding information from the bulk of the carbon layers, XPS and XAES possess a high surface sensitivity. The biocompatibility of the DLC coated vessels was tested in vivo using sheep. The vessels (30 cm length, 7 mm diameter) were coated in argon atmosphere (0.25 Pa) with DLC layers with different sp^3-C

contents and thicknesses. The preliminary results from all three sets tested in vivo (two thicknesses of "harder" and one of "softer" coatings) using eight sheep showed no substantial dependence on the type and thickness of the DLC layers.

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