Protective coatings for enhanced performance in biomedical applications

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Biomedical implants such as prosthetic hips and heart stents and instruments used *in vivo* all have negative performance issues. A common solution, which can also be appropriate for other devices, is to apply a diamond-like carbon thin film in order to enhance the performance of the devices. The films were produced by pulsed laser deposition and characterised by Raman spectroscopy, atomic force microscopy, ball on flat tribometry, contact angle measurements and spectrophotometry. The stability of the films was checked by soaking in simulated body fluid (SBF). The root mean square surface roughness was found to be <1 nm, and a coefficient of friction of 0·08 was produced in a lubricated environment. Contact angles ranged from 65 to 88°. The coatings produced on fused silica had high transparency and showed no delamination after 43 weeks of immersion in SBF. These films have potential to enhance the performance of biomedical implants and instruments.

Keywords: Coating, Biomedical, Carbon

Introduction

Coronary stents are devices surgically implanted into a patient's restricted artery to support the walls of the artery and allow greater blood flow. Two problems associated with stents are thrombosis, which is the formation of a thrombus or clot along the inside of the stent, and cytotoxicity, which is an unfavourable reaction of cells in the body to metal ions released from the stent material. Inert and hemocompatible, diamond-like carbon (DLC) has shown promise as a coating for reducing thrombosis and preventing cytotoxicity.[1] These films can also be used in conjunction with drug eluting materials to improve their effectiveness.[2]

Joint replacement surgery is a common surgical procedure to reduce chronic joint pain or replace a damaged joint. Wear and subsequent debris formation are two problems with today's joint replacement materials. Wear can lead to joint failure, causing revisionist surgery to be required, and wear debris from the prosthetic joint can accumulate in the body, causing adverse reactions. The DLC could potentially reduce wear and debris formation, making joint replacement safer and longer lasting.[3]

The bronchoscope is a medical device that can be used to inspect the airways of a patient's lungs, both the bronchi and the bronchioles. Within the lungs, a warm moist environment, the bronchoscope lens can fog over. The lens can be made antifogging by applying a solid transparent, superhydrophilic DLC coating, eliminating the need to apply a liquid surfactant.

Diamond-like carbon films are amorphous carbon films with a mixture of sp^2 and sp^3 hybrid bonding.[4] The DLC films can have properties similar to that of diamond, including high hardness, low coefficient of friction, optical transparency and chemical inertness.[5–11] These properties make DLC an ideal protective coating for such applications as automotive parts, optical windows, magnetic storage devices, microelectromechanical devices and biomedical implants and instruments.[12–14] In particular, it is thought that DLC can overcome late stent thrombosis, provide lower friction and higher wear rate in hip implants and be tailored for use on a bronchoscope lens as it can be made transparent through appropriate doping or deposition conditions.

The primary goal of this work is to explore the properties of DLC coatings to meet the desirable properties described above and understand the optimal parameters to meet the needs of biomedical implants and instruments.

The films were produced by pulsed laser deposition (PLD) on silicon, fused silica and silicon nitride substrates. Fused silica was used as this is a material appropriate for use in a bronchoscope lens. Silicon and silicon nitride were used as heart stents, and hip implants are commonly made of metal; in general, metal requires a bond coat usually in the form of silicon or its compounds, such as silicon nitride – using them directly eliminates a step in the screening process of DLC as an appropriate coating. Silicon nitride was selected as spheres were available, and this provided data with a curved surface. Characterisation was performed by

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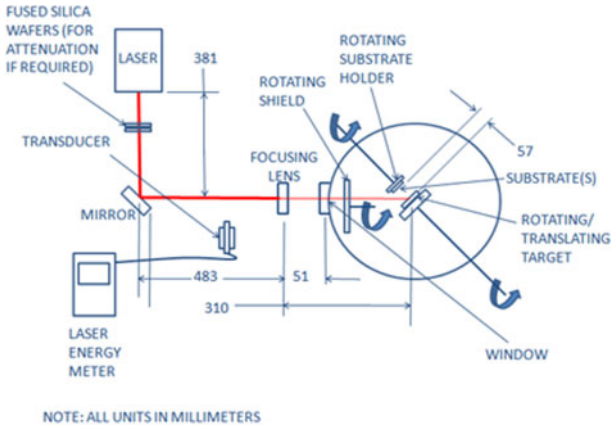


1 Schematic of PLD system

Raman spectroscopy for structural information, atomic force microscopy to determine surface roughness, ball on flat tribometry for elucidation of the friction coefficient, contact angle measurements to determine the hydrophobic/hydrophilic nature of the films, optical profilometry for thickness, spectrophotometry for transparency and soaking in simulated body fluid (SBF) to establish performance *in vivo*.

Experimental

Silicon, fused silica and silicon nitride have low surface roughness and repeatable properties. The silicon substrates were 450 μm thick, 25·4 × 25·4 mm squares, single side polished and in the (100) orientation. Each substrate was ultrasonically cleaned in acetone and methanol (in separate steps) followed by a 20 s dip in buffered oxide etch solution (6 : 1 volume ratio of 40%NH_4F in water to 49%HF in water). The fused silica substrates were UV grade, 500 μm thick, 25·4 × 25·4 mm squares. Each substrate was ultrasonically cleaned in acetone and methanol (in separate steps) followed by a 2 min dip in piranha solution (1 : 1 volume ratio of concentrated H_2SO_4 and 35% H_2O_2). Both silicon and fused silica substrates were rinsed with ultrapure water and dried with compressed argon or nitrogen after each step. The silicon nitride substrates were 12·7 mm diameter spheres. Before use, the silicon nitride spheres were ultrasonically cleaned in acetone for 10 min and then rinsed with ultrapure water before drying with compressed nitrogen. The process was repeated with methanol.

The DLC films were produced using a PLD system with an ArF excimer laser at a wavelength of 193 nm. The laser had a repetition rate of 50 Hz and a pulse length of 15 ns. The laser beam was focused onto a 51 mm diameter semiconductor grade graphite target, which was rotated and translated. The focused beam area was 0·13 mm^2. The substrates were affixed to a rotating holder for more uniform film coating. After initial rough pumping to 15 mtorr with a mechanical pump, a cryopump was used to pump the vacuum chamber to a pressure of $1·1 \times 10^{-6}$ torr or lower. For heated depositions, an incandescent lamp radiatively heated the backside of the substrate holder. A thermocouple in contact with the substrate holder was used to monitor the deposition temperature. A schematic of the laser and system optics is shown in Fig. 1.

The samples produced were divided into three groups, along with two special samples made for the soaking experiment and the tribological testing. The first group was DLC deposited on silicon with varying fluence and parameters shown in Table 1. The second and third groups were DLC deposited on fused silica with varying fluence and deposition temperature respectively, whose parameters are shown in Tables 2 and 3. PLD #36, the SBF soaking sample, was produced on four fused silica substrates at a temperature of 19°C at a fluence of 3·5 J cm^{-2} for a deposition time of 15 min. Sample PLD #11 was produced on three silicon nitride spheres and three silicon wafers at a deposition temperature of 200°C at a fluence of 4·2 J cm^{-2} with 4 h of deposition time. This deposition of DLC was preceded by the application of an intermediate silicon bond coating at 200°C with a fluence of 5·0 J cm^{-2} and 1 h of deposition time using a silicon wafer as the ablation material.

Film thickness was measured using an optical profilometer, which was a Phase Shift Technology Micro XAM surface mapping microscope (Tucson, AZ, USA) connected to a PC with MapVue AE 1·24·1 software. Measurements were made at a minimum of two locations per sample.

Raman spectroscopy was performed on all samples using a Renishaw inVia Raman microscope (New Mills, Wotton-under-Edge, Gloucestershire, UK). The laser was focused through a ×50 lens and had a power of 4 mW. The laser wavelength was 633 nm. Acquisition

Table 1 Process Parameters for DLC Produced on Silicon substrates for 240 minutes with varying Laser Fluence

Sample PLD #	Laser Fluence (J/cm^2)	Deposition Temperature (°C)
21	2·8	192
26	3·4	194
32	3·9	195
29	4·3	194
24	4·7	192

Table 2 Process Parameters for DLC Produced on Fused Silica substrates for 15 minutes with varying Laser Fluence

Sample PLD #	Laser Fluence (J/cm^2)	Deposition Temperature (°C)
47	1·8	18
44	2·2	17
43	2·6	21
42	3	19
41	3·5	18
40	3·9	20

Table 3 Process Parameters for DLC Produced on Fused Silica substrates for 15 minutes with Varying Deposition Temperature

Sample PLD #	Laser Fluence (J/cm^2)	Deposition Temperature (°C)
42	3	19
50	3·1	56
49	3·1	92
48	3·1	128
46	3·1	163
45	3·1	202

Table 4 Film Thickness and Deposition Rate for DLC Produced with varying Fluence on Silicon Substrates at 200°C Deposition Temperature for 240 (±2%) minutes

Sample PLD #	Laser Fluence (J/cm^2)	Thickness (nm)	Deposition Rate (nm/minute)
21	2·8	97±7	0·40±0·03
26	3·4	82±4	0·34±0·02
32	3·9	100±5	0·42±0·02
29	4·3	139±3	0·58±0·02
24	4·7	170±5	0·71±0·03

was for 10 s with 10 accumulations at each location measured.

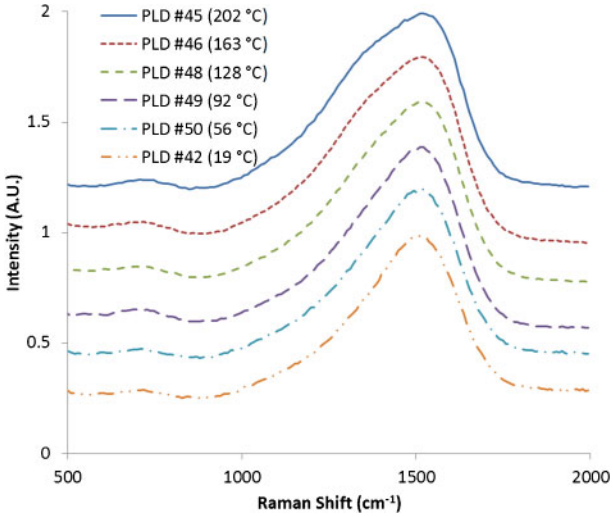
The SBF was prepared as described by Cho *et al.*[15] Samples were immersed in vials containing SBF and incubated at 36·5°C using a temperature controlled water bath. At varying time intervals, the samples were removed and photographed microscopically, then placed in fresh SBF and returned to the 36·5°C environment.

The topography of the samples was measured using a VEECO Nanoscope V atomic force microscope with a Nanoscope V controller (Plainview, NY, USA). The system was equipped with a nitrogen gas vibration isolation stage, an acoustic/Faraday cover, a Nanoscope V controller and a computer with Nanoscope 7·30 software installed. All images were taken under ambient conditions using silicon tips in tapping mode. Analysis was performed using WSxM 4·0 Beta 2·0 software.[16]

The contact angle of water on the samples was measured using a Krüss DSA20E Easy Drop Standard with a software controlled dosing system (Hamburg, Germany). Measurements were made at five locations per sample using the sessile drop method with a drop size of 2 μL.

Tribological sliding friction tests were made using samples from the PLD #11 deposition process using a ball on flat geometry. The test environments were dry nitrogen, air, Mobil 15W30 synthetic motor oil or bovine serum. Test duration and sliding speed were dependent upon sample performance.

Spectrophotometry data were obtained using a GenTech Scientific TU-1901 double beam ultraviolet/visible light spectrophotometer equipped with UVWin5·0 analysis software (Arcade, NY, USA). The transparency of DLC on fused silica substrates was measured between 190 and 900 nm at 1·0 nm intervals. The attenuation effects of the substrate were subtracted from the transmittance plots by using a bare fused silica substrate as reference during the measurements.



2 Raman spectra of DLC films deposited on silica substrates with varying deposition temperature at 3·1 J cm^{-2} fluence

Results and discussion

The thickness and deposition rate results for the DLC on silicon films are shown in Table 4. The film growth rate increased with increasing laser pulse energy, as expected, because increasing pulse energy and greater fluence values will increase the amount of carbon ablated with each pulse.

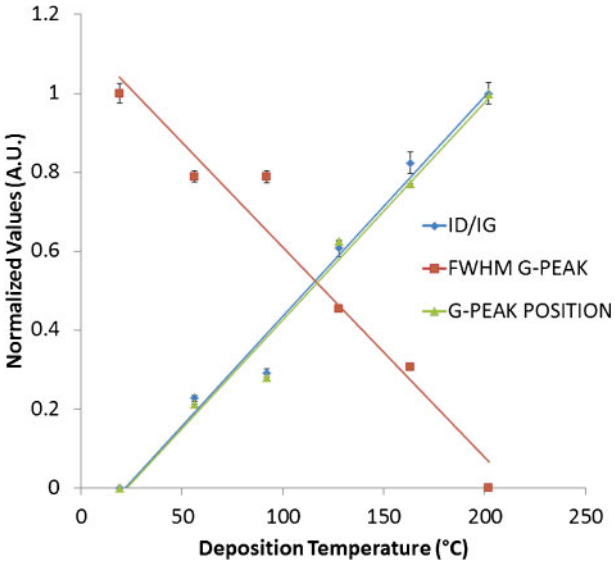
There is no apparent relationship between deposition rate and laser fluence or deposition temperature for the DLC films made on fused silica substrates.

Raman spectroscopy showed that the laser fluence had little effect on the structure of the DLC films on silicon or silica substrates; the deposition temperature, however, did have an effect, as seen in Fig. 2. At a deposition temperature of 202°C, the film's spectrum has a feature on the left side of the peak that gradually diminished with decreasing temperature. The Raman spectra for DLC films can be deconvoluted into two Gaussian peaks, known as the D peak and G peak, located at ~1360 and 1560 cm^{-1} respectively, when excited by visible light.[6] The relative intensity of these peaks (I_D/I_G) and the full width at half maximum and position of the G peak provide insight into the sp^3/sp^2 ratio of hybrid bonding in DLC films. However, Table 5 shows that different references present different trends. Deconvolution of the spectra in Fig. 2 into D and G peaks yielded the data in Table 6.

Table 5 Relationship between sp^3 Content, G-Peak Position, ID/IG, Full-Width Half-Maximum of the G-Peak, and Deposition Temperature in Literature

Author(s)	Year of Publication	sp^3/sp^2 bonding	G-Peak Position	I_D/I_G	FWHM G-Peak	Temperature (°C)
Balon[13]	2005	↑	↓	↓	↑	↓
Chhowalla[14]	2000	↑	↓	↓	↑	↓
Ding *et al.*[15]	2009	↑	↓	↓		
Ferrari/ Robertson[17]	2000	↑	↑	↓	↑	
Marchon[16] [a]	1997	↑	↓			↓
Paul[2] [a]	2008	↑	↑	↓	↑	
Reuter[18]	2006	↑	– –			

[a] The DLC films studied were hydrogenated.

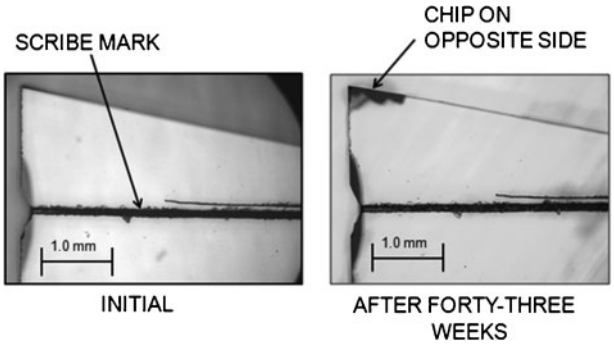


3 Normalised Raman spectra characteristics versus deposition temperature

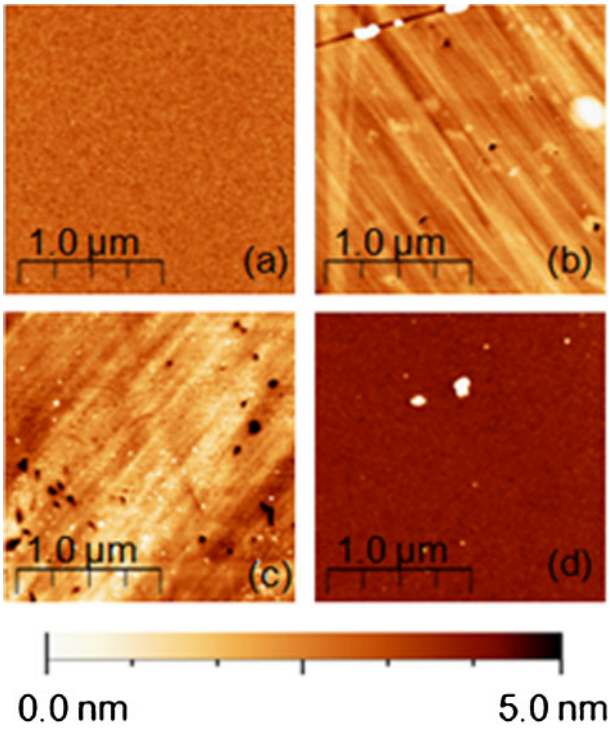
The ratio of intensities of the two peaks I_D/I_G, the full width at half maximum of the G peak and the G peak position were normalised and are shown graphically in Fig. 3. Interestingly, the full width at half maximum of the G peak grows in an inverse relationship with I_D/I_G and G peak, position which increases with deposition temperature. These relationships agree with the results of Balon *et al.*, Chhowalla *et al.*, Ding *et al.* and Marchon *et al.*, which suggest that the films produced become more diamond-like with decreasing temperature.[17–20]

To be biocompatible, a material must be stable within the human body. *In vitro* testing in SBF provides an inexpensive way to determine the stability of the DLC films. Sample PLD #36, which is DLC deposited on fused silica, is shown in Fig. 4 after 43 weeks of soaking in SBF. No change was observed in the film, even at the interface between the DLC and the fused silica exposed by a scribe mark that was made before soaking began. Any anomalies seen were attributed to handling damage and refraction effects at imperfections on the substrate edge.

Understanding the morphology and surface roughness of the DLC films produced is important for the biomedical applications being considered. For coronary stents, increased surface roughness can lead to increased platelet adhesion, which causes thrombosis. For artificial joints, increased roughness of the wear surface may result in a higher coefficient of friction and increased wear. Roughness can also affect the contact angle, so it must be considered when choosing a film to be used as a bronchoscope lens coating.[21]



4 Micrographs of DLC film, PLD #36, initially and after 43 weeks immersion in SBF

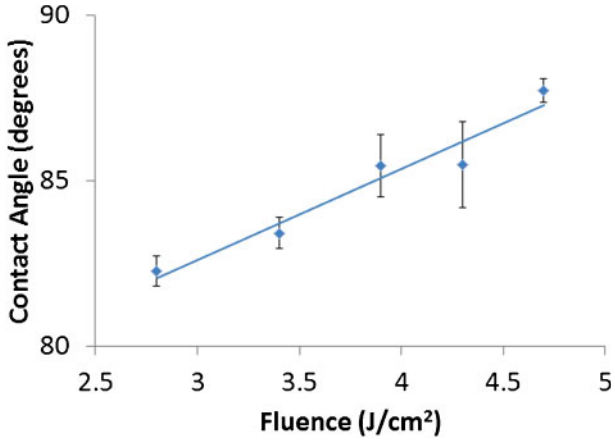


5 AFM images of DLC: *a* PLD #21 on silicon; *b* PLD #42 on fused silica; *c* fused silica; *d* silicon wafer

The morphology of the DLC films tended to vary greatly depending upon the substrate on which the film was deposited. A representative image for DLC deposited on silicon is shown in Fig. 5*a*, which reveals a disordered surface. The morphology of DLC deposited on fused silica is quite different, as shown in Fig. 5*b*, which has repeating striations running across the surface. These differences are most likely due to the

Table 6 Raman Spectra Characteristics for DLC Films made at Varying Deposition Temperatures at 3·1 J/cm^2 Laser Fluence

Sample PLD #	Temperature (°C)	G-Peak Position	I_D/I_G	FWHM G-Peak
45	202±1	1563·4±0·3	1·68±0·05	172·5±2·4
46	163±1	1557·4±0·3	1·52±0·05	186·5±2·4
48	128±1	1553·5±0·3	1·32±0·05	193·3±2·4
49	92±1	1544·4±0·4	1·04±0·04	208·7±2·4
50	56±1	1542·6±0·4	0·98±0·04	208·7±2·4
42	19±1	1537·0±0·9	0·77±0·04	218·4±2·4



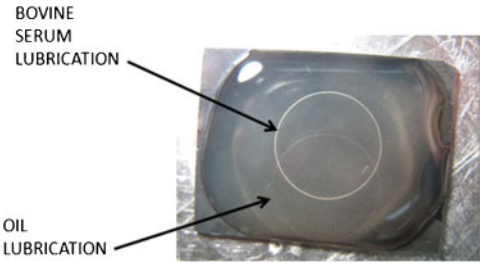
6 Contact angle as function of fluence for DLC films deposited on silicon substrates at 200°C deposition temperature

roughness of the underlying substrate. It is quite obvious after measurement that bare fused silica substrates have the same striations found on the samples of DLC deposited on fused silica, as shown in Fig. 5*c*. The striations are absent from the uncoated silicon substrates, as shown in Fig. 5*d*.

In general, the DLC films deposited on silicon were much smoother than those deposited on fused silica. Moreover, more variation in roughness was seen in the samples deposited on fused silica. Again, this variation is likely due to the effects of the substrate, as the fused silica substrates were generally rougher (rms roughness $>0{\cdot}7$ nm) than the silicon substrate (rms roughness $<0{\cdot}12$ nm). The results did not vary with laser fluence, deposition temperature and rms roughness.

It is important to understand the interaction that a biomaterial will have with its environment at the surface. The contact angle that water makes at the surface of a material is a quick way to estimate the surface energy of that material. High energy surfaces tend to be hydrophilic, achieving a high degree of wetting, while low energy surfaces tend to be hydrophobic, with water beading up on the surface. Contact angles have been measured for water on the surface of the DLC films to determine their potential for biomedical applications. For heart stent coatings, a low surface energy superhydrophobic coating is preferred to decrease the probability of platelet adhesion, which can lead to thrombosis or clotting in the artery. For bronchoscope lenses, a high surface energy superhydrophilic surface is required to make the lens antifogging.

Figure 6 shows contact angle as a function of laser fluence for a series of DLC films produced with varying laser pulse energy on silicon substrates with a deposition temperature of 200°C. The films show slightly increased contact angle with increased laser fluence, ranging from 82° at 2·8 J cm^{-2} to 88° at 4·7 J cm^{-2} as structure did not change as evident from the Raman spectra and surface roughness values were similar. For the films deposited on fused silica, no clear relation exists between laser fluence or deposition temperature and contact angle. All undoped films produced are neither strongly hydrophilic nor strongly hydrophobic with contact angles ranging from 65 to 88°; however, this can be changed by appropriate doping in future work.



7 Diamond-like carbon sample, PLD #11, after wear testing with bovine serum and oil lubrication

For the DLC coatings to be useful in artificial joints, they must have good wear properties. To this end, one of the DLC films, PLD #11, was tested under the conditions shown in Table 7.

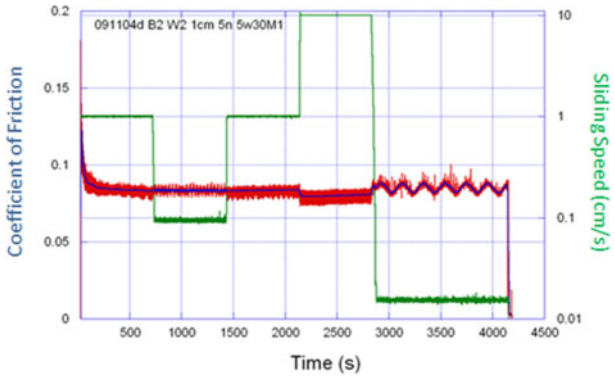
The DLC film tested under dry sliding conditions in both dry nitrogen and air showed delamination. Large wear scars were produced in both environments. The DLC film tested by the ball on flat tribometer with oil lubrication exhibited very light markings with no noticeable wear debris, as shown in Fig. 7. The coefficient of friction for the DLC film with oil lubrication as a function of time and sliding speed is shown in Fig. 8. After an initial wear-in period, the coefficient of friction stabilised at $0{\cdot}08 \pm 0{\cdot}01$. The film maintained this low coefficient of friction during the remainder of the testing at each of the varying sliding speeds. The film's performance was typical of DLC in a lubricated environment.[22] Lubrication with bovine serum yielded a wear track with noticeable debris. This result does not bode well for the application of hip joints at this juncture.

For the films to be useful as protective coatings for bronchoscope lenses, they must be transparent. The DLC films produced are partially transparent, as can be seen in Fig. 9. Figure 10 shows that transmission is reduced with increased laser fluence, which could be due in part to the higher deposition rate at larger fluences, leading to thicker films and more attenuation. The thickness results from the profilometry section do not appear to support this hypothesis, however. As shown in Fig. 11, decreased deposition temperature leads to

Table 7 Tribological Test Parameters and Resulting Coefficients of Friction for DLC against DLC, PLD#11

Environment	Load (N)	Coefficient of Friction at Steady State	Sliding Speed (cm/s)	Test Duration(s)
dry nitrogen	5	n/a – film failure	1	3400
air[b]	5	n/a – film failure	1	140
oil[c]	5	$0{\cdot}08 \pm 0{\cdot}01$	0·02, 0·1, 1, and 10	4200
bovine serum	5	n/a – film failure	0·4 and 0·1	2400

[b] at 21% relative humidity
[c] Mobil 1 5W30 synthetic motor oil



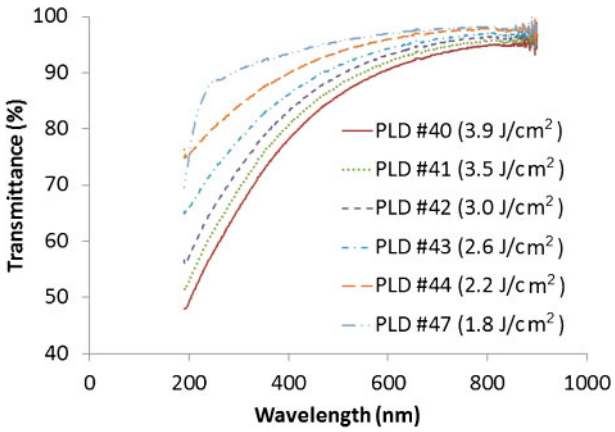
8 Coefficient of friction during DLC against DLC wear testing with varying sliding speeds as function of time with oil lubrication

9 Transparent DLC

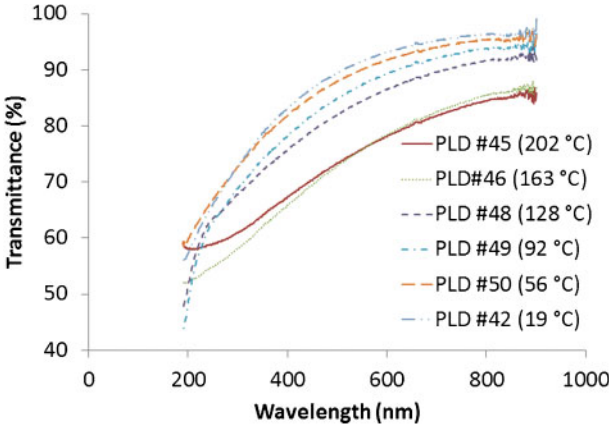
increased transmission. This trend is likely due to a change in the structure of films, as can be seen in the Raman spectroscopy results in Fig. 2 and Table 6. The results suggest the films become more diamond-like with greater sp^3 content and an increasing band gap with decreasing temperature. In general, the films allow good transmission of light in the infrared and visible wavelengths. Transmission reduces rapidly at ultraviolet wavelengths, however.

Conclusion

Diamond-like carbon thin films were successfully produced on silicon, fused silica and silicon nitride substrates using a PLD system. Raman spectroscopy showed that the structure of the films was dependent



10 Transmittance of DLC films made with varying fluence at 20°C deposition temperature



11 Transmittance of DLC films made with varying deposition temperature at 3·1 J cm^{-2} fluence

upon the deposition temperature but independent of the laser fluence. The films were stable after 43 weeks immersion in SBF at 36·5°C, showing no delamination during that time when viewed microscopically. Contact angles for water on the surface of these films varied between 65 and 88°. The films produced were very smooth with rms roughness values of <0·35 nm when deposited on silicon, although larger values occurred when the film was deposited on rougher fused silica substrates. Ball and flat tribometry showed these films to have excellent wear resistance and a low coefficient of friction (0·08) in an oil lubricated environment. Spectrophotometry showed that these films have good transparency in infrared and visible light.

The results showed that the films have potential for longevity *in vivo* but did not operate well in a high friction environment in bovine serum. The smoothness, contact angle and transparency show potential in the area of heart stents and particularly as a coating for bronchoscope lens. The latter application will be part of a more detailed study in future work. A different type of deposition mechanism is recommended for high friction environments such as hip, knee and shoulder joint prostheses.

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