Sticking non-stick: Surface and Structure control of Diamond-like Carbon in Plasma Enhanced Chemical Vapour Deposition

B J Jones\textsuperscript{1,2} and N Nelson\textsuperscript{3}

\textsuperscript{1} School of Materials, University of Manchester, Oxford Road, Manchester M13 9PL UK
\textsuperscript{2} School of Applied Sciences, University of Huddersfield, Queensgate, Huddersfield, West Yorkshire HD1 3DH UK
\textsuperscript{3} School of Engineering and Design, Brunel University, Kingston Lane, Uxbridge, Middlesex UB8 3PH UK

E-mail: b.j.jones@physics.org

Abstract. This short review article explores the practical use of diamond-like carbon (DLC) produced by plasma enhanced chemical vapour deposition (PECVD). Using as an example issues relating to the DLC coating of a hand-held surgical device, we draw on previous works using atomic force microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy, scanning electron microscopy, tensiometry and electron paramagnetic resonance. Utilising data from these techniques, we examine the surface structure, substrate-film interface and thin film microstructure, such as sp\textsuperscript{2}/sp\textsuperscript{3} ratio (graphitic/diamond-like bonding ratio) and sp\textsuperscript{2} clustering. We explore the variations in parameters describing these characteristics, and relate these to the final device properties such as friction, wear resistance, and diffusion barrier integrity. The material and device characteristics are linked to the initial plasma and substrate conditions.

1. Introduction

A low-friction, hard-wearing, biocompatible, barrier thin-film material, diamond-like carbon (DLC) contains both sp\textsuperscript{2} (graphitic) and sp\textsuperscript{3} (diamond-like) bonded carbon atoms, and often a significant level of hydrogen. Medium-range order, clustering of the sp\textsuperscript{2} bonded atoms within a sp\textsuperscript{3} matrix, plays a substantial part in the properties of the material. Tuning the balance of the constituents, phases and ordering allows the creation of a material with properties that can be tailored to match requirements resulting in application in many areas including electronics [1], aerospace [2], and medical devices [3] as well as beer storage [4].

Plasma enhanced chemical vapour deposition (PECVD) is a widely used laboratory technique for DLC deposition. This work reviews research utilising micro and nanoscale characterisation techniques in order to understand the effects of production processes and improve film quality and function for the end user. Application of methods such as electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) has enabled improved understanding of the changes in film structure, surface and properties with variation.
of plasma conditions. This includes work to improve film adhesion [5], create machining tools with improvement in lifetime and reduction in power consumption [6], and enhance the thin film diffusion and surface properties to facilitate production of improved medical tools and implants [3,7].

This short review paper examines factors affecting PECVD deposited DLC structure and properties by exploring some issues associated with the coating of surgical device, figure 1 [3,7].

![Diamond-like carbon coated aluminium surgical assist device. Reprinted from Diamond and Related Materials [7] copyright (2010) with permission from Elsevier.](image)

2. Plasma control

The rf power supplied, or negative self bias induced, may be the primary method within a single PECVD system with which to control the deposition energy of ion species. By increasing the bias voltage the film structure can be adjusted from hydrogen-rich polymeric coating, to sp$^3$-rich diamond-like carbon to a more graphitic-like carbon. The optimum structure will be related to the application, the different films have varying defect densities and diffusion barrier properties, as well as friction and wear characteristics [1,2,7,8]. For example, Zolgharni et al. [6] use an Ar/C$_2$H$_2$ precursor and show an optimum bias voltage of 400-550V for friction and wear in pin-on-disc tribological tests, and 450V for coating of drill bits used for dry machining of aluminium. For the surgical device, a lower bias of 200V is optimal for diffusion barrier properties [7].

However, the ion energy and species distribution are also affected by factors such as precursor gas mix, chamber pressure, and substrate or cathode structure [9-11]. For example, varying the Ar/C$_2$H$_2$ balance of the precursor gases affects the film surface structure, as shown by AFM analysis where average roughness increases from 2.6nm to 5.0nm and peak density decreases from approximately 50 to approximately 12 peaks per square micron, as the argon content of the precursor gas mix is raised from 0 to 45% [11] as shown in figure 2. In addition the clustering of the sp$^2$ regions increases with increasing Ar in the precursor mix, as observed by electron paramagnetic resonance (EPR), leading to an increase in film conductivity [11]. It is postulated that the changes in the film structure are related to the balance of impinging species affecting film nodulization and sp$^3$/sp$^2$ ratio related to the balance of surface diffusion and subplantation and relaxation of internal stresses [11-13]. These structural
changes lead to an optimal argon content for a particular application, relating to properties such as friction or material adhesion in dry drilling [6,11] or adherence of biofilms for medical devices [3,7].

Figure 2. Atomic force microscopy images and calculated texture parameters of DLC on silicon showing changes to the surface structure with increasing argon content of precursor gas mix. Reprinted from Diamond and Related Materials [11] copyright (2008) with permission from Elsevier

The film chemistry and structure can be affected by incorporation of species via the precursor gas mix [3,7,14,15], or post treatment processes [1,16,17]. For the medical assist instrument [7], in addition to limiting adherence of biofilms, the primary purpose of the DLC was for diffusion barrier properties, to protect the instrument from biofluid corrosion and to protect the patient from exposure to aluminium. Barrier properties were optimised by incorporating silicon into the film, through the inclusion of tetramethylsilane (TMS) in the precursor gas mix. Aggressive erosion tests through immersion of test pieces in sodium hydroxide for 30mins showed a precursor ratio TMS: C\textsubscript{2}H\textsubscript{2} of 1:4 optimal for barrier properties, resulting in a 53\% reduction in aluminium transfer against an uncoated sample, and 45\% reduction versus an unsilicated amorphous carbon. The results are also correlated with an increase in water contact angle, reflecting the behaviour of fluid at the film surface [7] and are summarised in figure 3. The incorporation of silicon to improve the diffusion barrier properties is consistent with that seen by other groups [14,15] and may be related to increased hydrogen and sp\textsuperscript{3} fractions in the film [14,5].

3. Substrate effects
Factors relating to the substrate also affect the flux, energy, species and interactions of depositing ions and strongly affect the resultant film structure. Although PECVD is a non-line of sight process, and has been described as producing uniform films over large areas, the structure of many devices to be coated, such as the medical assist device [7] are not uniformly planar and may perturb the plasma, leading to variations in the deposited film. Nelson et al [9] show how substrate geometry may affect the DLC film, by exploring variation in the deposited roughness, R\textsubscript{s} of 307±47 nm over 10x10 \textmu m, compared to 29.4±2.7 nm for the film deposited on steel, film with the orientation of the substrate, using silicon as a model surface.
Figure 3. Effect of silicon content of precursor (TMS) on film barrier properties, characterised by transfer of aluminium in NaOH immersion, and water contact angle. Data from [7].

Figure 4. Effect of substrate orientation and geometry on DLC surface texture. Surface parameters and example AFM images for vertically orientated surface (top right, □) and horizontally orientated surface (lower right, ▲). Note the difference in z-scale. Reprinted from Surface and Coatings Technology [9] under creative commons http://creativecommons.org/licenses/by/3.0/legalcode
They show variation in film roughness ($R_a$) of a factor of over 30, increasing from 0.4nm on a horizontal sample, to 15nm at the top of a vertically positioned sample, figure 4. Film thickness varies by a factor of 2 and variation is exhibited in the nodularity and $sp^2/sp^3$ ratio, assessed through Raman spectroscopy, over a lateral or vertical scale of approximately 10mm. This is linked to the inhomogeneous distribution of ion species within the plasma and to field concentration at the sharp vertical edge, affecting plasma sheath formation and shielding effects, leading to variation in effective energy, flux and species of the impinging ions, and therefore to variation in surface diffusion and subplantation mechanisms in the film growth [9]. These factors ultimately affect the friction and critical load of the device [9].

![DLC Produced](image)

**Figure 5.** DLC produced with the same nominal parameters on (a,b) epoxy resin and (c,d) concurrently produced on stainless steel and (e,f) separately produced on stainless steel, over (a,c,e) 10x10µm and (b,d,f) 1x1µm, showing variation of DLC structure with substrate material. Copyright © 2012 John Wiley & Sons, Ltd. Reproduced from [18], with permission.

Atomic force microscopy studies of DLC deposited on epoxy resin in comparison to steel for application to aircraft landing gear [2,18] clearly show the differences between nominally similar coatings on radically different substrates, figure 5. Although the DLC deposition conditions are similar to those optimized for machining of aluminium [6] the film on epoxy has a root mean square
the skewness and kurtosis of these surfaces also exhibit differences, but perhaps the most significant change in surface texture is indicated by the peak density, $0.12 \, \mu m^{-2}$ on epoxy compared to $1.1 \, \mu m^{-2}$ on steel, reflecting differences in the surface diffusion of the depositing species [18].

The chemistry of the film surface is also altered. The $sp^2/sp^3$ ratio can be calculated via Raman spectroscopy, as above, [9], however, other works utilise XPS to examine the surface microstructure. Analysis techniques may focus on C1s deconvolution [5,18] or X-ray excited auger spectroscopy measurements [18,19]. XPS results show that the $sp^2$ fraction of the film on epoxy is higher than that of the DLC on steel, by 3-8 abs.%, though the exact figure depends on calculation procedure [18]. These differences in the film structure, in addition to the variation in modulus and interface adhesion, lead to variation in the device performance, the DLC+Epoxy combination performing better in wear and friction tests for applications to aircraft landing gear [2,18].

The presence of substrates with a high degree of volatility, or which are easily sputtered, also affects the gas mix of the plasma, and subsequent film structure. The research on DLC coated on epoxy and steel [18] demonstrates transfer of Ca, Na, N and O from the epoxy resin structure into the DLC film deposited on steel within the same deposition period, suggesting transfer of components of the epoxy to the gas phase through heating, sputtering or outgassing, and subsequent deposition with the DLC [18].

4. Interface region

The adhesion of the DLC film to the substrate material or device is of high importance, failure of the film adhesion can lead to catastrophic failure of the device, for example in a biomedical implant. Although the film is biocompatible [20], film failure may lead to an adverse reaction in the patient to the underlying metal surface, or enhancement of aseptic loosening process of an implant as a result of debris from the film [3], or for some titanium-DLC films, debris may be internalised in bone marrow [21]. The epoxy structure discussed above is an example of a thick interlayer that improves adhesion [2], many groups have utilised interlayers to improve adhesion of diamond-like carbon to a substrate, this may be metallic such as tungsten [22] or, often in adherence to steels, based on a graduated silicon layer [5,6,9,11]. In addition the substrate cleaning process is highly important, and many teams use an argon plasma pretreatment step; however, earlier work [5] highlights that the pretreatment conditions vary significantly in terms of power and duration. The argon plasma treatment step has a dual purpose, at low power the substrate is cleaned through the removal of hydrocarbon contamination [5]; however, in a study on 304 stainless steel substrates [5] XRD and XPS analysis, coupled with electron microscopy, show that at higher powers the argon plasma processing restructures the metal surface, preferentially removing chromium from the top layer and generating a nanotextured, nanocrystalline surface, figure 6.

This processing improves film adhesion in bend tests by approximately three orders of magnitude [5]. However, the DLC structure is also affected by the changes to the substrate, as suggested in section 3 above. In this instance the rms surface roughness, $R_q$ is reduced, from 37 nm to 21 nm and the nodularity of the surface is altered, as shown in figure 7. The $sp^2$ fraction of the DLC surface is also affected by the microstructured interface [5]. Failure to adequately pretreat the substrate surface can lead to rapid film delamination, figure 8.
Figure 6. 304 Stainless steel with a) sonication preclean and argon pretreatment with bias voltages of b) 300V c) 450V and d) 600V. Higher magnification images of e) 450V and d) 600V reveal nanotextured surface. Reprinted from *Diamond and Related Materials* [5] copyright (2011) with permission from Elsevier.

Figure 7. Scanning electron microscopy images of DLC films deposited on substrates with argon plasma pretreatment of a)300V, b) 450V and c)600V showing effects of substrate structure on DLC texture. Reprinted from *Diamond and Related Materials* [5] copyright (2011) with permission from Elsevier.
5. Conclusions
In this short review of previous work, issues affecting diamond-like carbon produced by plasma enhanced chemical vapour deposition have been briefly examined. Deliberate control of the plasma conditions, for example through rf power or negative self bias voltage, precursor gas mix or pressure, may cause variation in depositing in species or energy, leading to changes in the surface interaction mechanism and variation in the film structure and chemistry. In addition, other factors, such as substrate material, outgassing, contamination, and substrate shape, can lead to significant variation in effective energy and flux of impinging ions, as well as predominant ion species. These factors strongly influence film production, film structure and resultant properties, such as integrity of diffusion barrier, friction, wear and adhesion. Substrate interactions are therefore important to consider in DLC production and also have relevance to other PECVD materials such as silicon dioxide based films.

![Figure 8](image)

**Figure 8.** Unstuck non-stick: Failure to adequately prepare the substrate leads to film delamination.

Acknowledgements
Thanks to Lorna Anguilano, Tony Anson, Bob Barklie, Bob Bulpett, Joe Franks, Arun Mahendrun, Jesus Ojeda, Sander Podgoric, Richard Rakowski, Alan Reynolds, and Massoud Zolgharni. We gratefully acknowledge support of the Engineering and Physical Sciences Research Council, Technology Strategy Board, The Royal Society and the University of Huddersfield.

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