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# Environmental Impact of Physical Vapour Deposition and Plasma-Enhanced Chemical Vapour Deposition Technologies for Deposition of Diamond-like Carbon Coatings for Green Tribology

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Abstract: With low friction and high hardness, diamond-like carbon (DLC) coatings are a prominent surface engineering solution for tribosystems in various applications. Their versatility stems from their varying composition, facilitated by different deposition techniques, which affect their properties. However, environmental impact is often overlooked in coating design. The objective of this paper is to assess the resource efficiency of four different common deposition techniques, thus identifying critical factors for sustainable DLC deposition. The coatings were deposited in one single chamber, enabling a direct comparison of the resource consumption of each technology. Expenditure of electric energy and consumables per volumetric output accounted for the environmental impact of manufacturing the coatings, which was evaluated across the indicators of damage to human health, damage to ecosystems, and resource scarcity. Electric energy use, dictated by deposition rate, was demonstrated to be the most significant factor contributing to the environmental impact. The environmental impact of PECVD and  $\mu$ W-PECVD was comparable and remarkably lower than that of dcMS and HiPIMS, the latter being the least energy efficient process, with the lowest output rate but highest energy expenditure. Thus, µW-PECVD could be considered the 'greenest' production method. These findings are consequential for coaters to efficiently produce good-quality DLCs with low environmental impact.

Keywords: diamond-like carbon; PVD; PECVD; HiPIMS; environmental impact analysis

# 1. Introduction

Diamond-like carbon (DLC) coatings have been proven to be a remarkable choice in a vast range of applications at the industrial scale [1], and thus are an eminent green surface engineering solution to control the extent of wear and frictional losses of tribological systems. With low friction and hardness as high as 90 GPa [2], the great versatility of DLC arises from the extent to which its atomic composition can vary in terms of fractions and the configuration of the different carbon bonds, subsequently affecting its properties. As seminally illustrated by Ferrari and Robertson [3] on the ternary phase diagram, amorphous carbons can have any mixture of sp<sup>3</sup> (diamond-like), sp<sup>2</sup> (graphite-like), and even sp<sup>1</sup> sites, in addition to up to 60 at.% hydrogen [4]. The tetrahedral sp<sup>3</sup> bonds are responsible for the high elastic modulus and mechanical hardness, among other physical properties, of diamonds [5]. In turn, it is the conversion of the sp<sup>3</sup> structure into an sp<sup>2</sup> structure, i.e., graphitisation, that promotes the low-friction mechanism of DLCs [6]. Therefore, the



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Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/ licenses/by/4.0/). proportion of sp<sup>2</sup>/sp<sup>3</sup> bonded carbon and the degree of clustering of the sp<sup>2</sup> phase [7] are determinant parameters of the physical properties and tribological performance of amorphous carbon materials.

This diversity stems from the equally diverse deposition techniques available and their tuneable settings, which significantly influence the properties of coatings [8–10] and can be optimised for state-of-the-art outcomes. Substrate bias voltage [8,11,12] and temperature [13], cathode power [14,15], working pressure [8,14,16–19], and precursor [10,20] and process gas [21–23] compositions are commonly found as the most significant parameters contributing to the growth mechanisms and properties of carbon-based films. On top of that, different deposition techniques altogether beget compositionally equal coatings with different properties [24,25]. Dini [26] demonstrated that there is no particular coating technique that is superior in all scenarios.

For instance, direct current magnetron sputtering (dcMS) is the simplest and least expensive way to operate a magnetron [27]. Moreover, the sputtering source can be an element, alloy, mixture, or a compound; that is, it does not require specialized precursor materials. Drawbacks of this technique include high compressive residual stresses [26] and the production of porous coatings with a columnar microstructure [28] due to low metallic ion flux towards the substrate.

A sputtering configuration developed more recently to tackle the low quality of conventional MS coatings is High-Power Impulse MS (HiPIMS), which features a greater ionization rate, as well as self-sputtering and a lower deposition temperature, subsequently producing high-quality coatings with a denser structure, smoother morphology, higher hardness, and better adhesion properties [27]. This is enabled by employing pulsed plasma discharges with higher peak power densities that remain below the power limit for target or magnetron damage [28]. Albeit, HiPIMS also has low deposition rates [29,30].

Contrastingly, in plasma-enhanced chemical vapour deposition (PECVD), plasma induces or enhances decomposition and the reaction of the gaseous precursor species by means of glow discharge. This means that CVD processes require suitable precursors; in the case of DLC, gases that can be used are hydrocarbons such as  $CH_4$ ,  $C_2H_4$ ,  $C_2H_2$ ,  $C_4H_{10}$ , etc. [20,31,32]. Deposition temperatures are comparable to the low temperatures of sputtering processes—typically ranging from room temperature with no intentional heating to additional heating up to 350 °C. Furthermore, PECVD produces films with a high packing density (~98%), i.e., the deposited atoms are packed together compactly, which can determine the hardness of amorphous coatings [33], whilst providing substantially higher deposition rates and more uniform coatings of substrates with various shapes, including 3D [34,35], in comparison to sputtering, a 'line of sight' process can be used in which sputtered atoms require a direct path to be deposited on the exposed substrate. Moreover, a higher frequency power source for PECVD such as microwave ( $\mu$ W-PECVD) introduces more energy into the system, leading to a higher ionisation density and thus higher deposition rates [36,37].

It is important to point out that even more techniques are available to deposit DLC, such as ion beam-assisted sputtering, cathodic vacuum arcs, pulsed lasers [38], and high-pressure methods such as those using dielectric barrier discharge plasma [39]. Taking the above information into account, the disparities amongst the range of available techniques for coating deposition make it evident that an accurate assessment of the environmental impact of deposition techniques is a complex task. Studies by Igartua et al. [40] and Liu et al. [41] demonstrate the importance of associating performance assessment with environmental impact analysis. Works such as Klocke et al. [42] and Gassner et al. [43] quantified the mass throughput and the main energy-consuming process steps for coatings

deposited by using different techniques. This approach allows for precise identification of the most significant aspect of deposition to be optimised in terms of resource efficiency.

Nonetheless, these works perform a comparison between different 'end-product' coatings, rather than attempting to determine the most sustainable process overall to obtain the coating with optimum properties and performance. This paper evaluates the resource efficiency of pure DLC coatings deposited by using different techniques, namely dcMS a-C, HiPIMS a-C, PECVD a-C:H, and  $\mu$ W-PECVD a-C:H, and the resulting coating properties. The nomenclatures a-C and a-C:H refer to hydrogen-free and hydrogenated amorphous carbon coatings, respectively. The objective of this work is to identify the critical factors for sustainable DLC deposition.

# 2. Materials and Methods

The coatings were all deposited in the same chamber, which facilitates a direct comparison of the resource consumption of each technology. Expenditure of electric energy and consumables (cathode target or precursor gas and working gases) per volumetric output rate accounted for the environmental impact evaluation of each technique. To verify their optimised properties relevant to their tribological performance, the deposited coatings were characterised in terms of the following: thickness, morphology, surface topography, adhesion, atomic structure, hardness, and elastic modulus.

Further details on the methodology are presented below.

#### 2.1. Coating Deposition

The deposition methods utilised a bespoke Flexicoat 850 coating platform (Hauzer Techno Coating, Venlo, the Netherlands)—illustrated in Figure 1. The substrate holder table lies approximately 160 mm from the sputtering targets (600 mm  $\times$  125 mm) in the cathodes on opposing walls. The substrate used was quenched and tempered 100Cr6 steel discs which is a chromium-containing low-alloy high-carbon steel. The substrate hardness and elastic modulus as measured by nanoindentation were 12  $\pm$  1 GPa and 241  $\pm$  15 GPa, respectively, whilst the macrohardness was 61.5  $\pm$  0.1 HRC. The samples were polished to a surface finish of Sq = 9  $\pm$  2 nm (root mean square roughness Sq measured by white-light interferometry) and ultrasonically cleaned prior to deposition.



Figure 1. Schematic of Hauzer Flexicoat 850 system—top view (adapted from [37]).

For sputtering deposition, a graphite (99.995% purity) target was fitted on the source that has both unbalanced magnetron sputtering and HiPIMS capabilities. For the adhesion interlayer, a Cr target was fitted on the other cathode, equipped with magnetron sput-

tering only. For  $\mu$ W-PECVD only, in addition to the Cr target, a WC target was used for the interlayers.

The deposition steps for every technique are outlined in Figure 2 (in the lower levels of the steps, the specificity of the process is itemized) and detailed in the following. The systems that were taken into account in the energy consumption calculations are specified in the last column, namely heating power (hot-wall chamber system), bias power supply, and cathode, anode, or coil power supply where applicable, in addition to pumping energy. The energy due to base pumping, target cleaning, and substrate plasma etching was considered equal for every technique, given that these steps are not particular to any coating but depend on the conditions of the chamber and substrate. Moreover, the consumption of materials, i.e., process gases and carbon cathode target, was also taken into account. The main deposition condition measurands, including power, gas flow, pressure, temperature, etc., were monitored directly from the machine controller.



**Figure 2.** Sequence of process steps of DLC deposition (green markers show which deposition technique each step applies to).

First, pumping the chamber to create a base pressure vacuum ( $4 \times 10^{-5}$  mbar) was necessary in order to purge it of contaminant gases, such as oxygen and water vapour. During this step, for the dcMS, PECVD, and  $\mu$ W-PECVD processes, heating was also employed so that DLC deposition eventually occurred at the desired chamber temperature, based on previous results in the literature. The desired temperature is circa 120 °C for dcMS [13,44,45] and below 200 °C for both PECVD and  $\mu$ W-PECVD [32,46,47]. It is important to highlight that heating during DLC deposition was only utilised for dcMS in order to maintain the desired temperature, which was kept at 124 ± 9 °C during all steps. Meanwhile, for both PECVD processes, heating only during the pumping step was necessary and sufficient for the chamber to reach a temperature favourable for ionization [38], whereas no additional heating during DLC deposition was used to control the temperature below the desired threshold. The temperatures during DLC deposition via the PECVD and  $\mu$ W-PECVD processes were 162 ± 10 °C and 161 ± 26 °C, respectively, maintained by the plasma power.

The following steps included target cleaning by pre-sputtering and plasma etching of the substrate to clean the surfaces of contaminants, such as oxides and moisture, and to ensure better coating quality and adhesion. Subsequently, a ~0.8  $\mu$ m thick (Cr, Cr/C) interlayer was deposited by means of dcMS to ensure adhesion of the dcMS, HiPIMS, and PECVD DLCs. On the other hand,  $\mu$ W-PECVD DLC required a more robust (Cr, Cr/WC,

W-C:H) interlayer totalling ~1  $\mu$ m thickness, wherein Cr and Cr/WC were sputtered and co-sputtered, respectively, by means of dcMS, whereas the carbon in W-C:H originated from acetylene via a reactive MS process. This was needed, because, with the simpler (Cr, Cr/C) interlayer,  $\mu$ W-PECVD a-C:H completely delaminated immediately after deposition due to the higher internal stresses in the coating that were induced at the higher deposition rates achieved by  $\mu$ W-PECVD [32].

The penultimate step consisted of an adjustment particular to each process. In the cases of dcMS and HiPIMS, the holder where the substrates were fixed was placed facing the cathode and was kept still during DLC deposition. For both PECVD processes, it was necessary to adjust the pump speed, as a lower pumping speed limits the flow of processing gases [48], thus facilitating the higher working pressure required.

The final step was DLC deposition following the parameters shown in Table 1. Note that, whilst both dcMS and microwave sources were power-controlled directly, the HiPIMS source was voltage-controlled, along with controlling the tuneable pulse frequency, pulse duration, and charge. Meanwhile, the 4 coils that provide power to the PECVD process were current-controlled. Thus, the HiPIMS cathode power and PECVD coil power in the table are the resulting average power throughout the deposition. A 45-min delay followed by an increase over 15 min in the application of the substrate bias in the HiPIMS process was necessary to ensure better coating adhesion.

**Table 1.** Deposition parameters of DLC step with each technique.

Process	t <sub>tot</sub> [min]	t <sub>DLC</sub> [min]	s [%]	V [sccm]	p [Pa]	Q [°C]	UB [-V] (Mode)	n [rpm]	P [kW]
dcMS	275	90	100	165 (Ar)	0.40	120	200 (PLS)	0	3 (DC + PLS)
HiPIMS	365	180	100	300 (Ar)	0.59	-	150 (DC)	0	4.7, avg.
PECVD	290	90	66	270 (C <sub>2</sub> H <sub>2</sub> )	1.2	-	740 (PLS)	1.5	$4 \times 0.060$ (coil current 4 A)
μW-PECVD	295	60	72	pressure controlled (C <sub>2</sub> H <sub>2</sub> ), 350 (Ar)	1.2	-	240 (PLS)	2	2 × 2.0

 $t_{tot}$ : total process time;  $t_{DLC}$ : DLC deposition time; s: pumping speed; V: gas flow; p: working pressure; Q: heating temperature; UB: bias voltage; PLS: pulsed; n: table speed; P: plasma source power.

# 2.2. Coating Characterisation

The coatings were characterised with regards to their morphology, thickness, surface texture, adhesion, atomic structure, and mechanical properties, which are relevant to their tribological applications. The characterisation aimed to verify that the comparison was made between coatings that were fair representatives of each deposition technique, i.e., that their properties were the optimum of what could be achieved in the chamber used, especially in terms of hardness, thus ensuring that the findings of this study are meaningful.

We used scanning electron microscopy imaging with an JEOL JSM-5310 microscope (Oxford Instruments, Abingdon, United Kingdom) equipped with a tungsten filament. This allows for a qualitative analysis of coating structural morphology, which influences the mechanical properties and can be correlated with the deposition technique [25]. The thickness of the coatings was measured from the SEM images of their cross-section; the coatings were also deposited on a Si (100) wafer, which was then snapped to reveal the cross-section of the coating. The surface topography of the coatings was determined by white-light interferometry using a NPFlex 3D optical profiler (Bruker, Billerica, MA, USA), measured over an area of  $0.4 \times 0.4$  mm<sup>2</sup> and repeated at least 4 times for each sample, applying Gaussian Regression filter correction with a long-wavelength cut-off Lc = 0.08 mm.

Coating adhesion was evaluated by using the Daimler–Benz Rockwell C method [49], applying 150 kgf for 2 s, as well as by scratch testing, in accordance with the British Standard EN ISO 20502:2016 [50]. A Rockwell diamond indenter tip (200  $\mu$ m radius) was used with the following parameters on all samples: a progressively increasing load of 0–100 N, a loading speed of 100 N/min, and a scratching speed of 5 mm/min. A reduced scratching speed was necessary due to space restrictions on the sample.

A Renishaw Raman spectrometer (Renishaw, Wotton-under-Edge, United Kingdom) with a 488 nm wavelength laser was used to characterise the atomic structure of the coatings. The mechanical properties of the coatings were measured by nanoindentation according to BS EN ISO 14577–1:2015 [51] and BS EN ISO 14577–4:2007 [52]. Hardness and a reduced elastic modulus are produced from the load vs. displacement curve on the Micro Materials NanoTest NTX platform using a Berkovich diamond tip. The results were obtained from 100 indents of fixed depth which did not exceed 10% of the coatings' thickness in order to minimize the effect of the substrate on the elastic response [53]. The sample material Young's modulus was calculated from the reduced modulus according to the Oliver–Pharr method [54]. The hardness-to-elastic modulus ratio (H/E) of the coating, which physically represents deformation relative to yielding [55], directly correlates to its maximum tensile elastic stress and thus to its wear rate [56].

#### 2.3. Cradle-to-Gate Environmental Impact

Life cycle assessment (LCA) systematically addresses the potential environmental impact of product systems, from the raw material to final disposal. It comprises four phases: goal and scope definition, inventory analysis, impact assessment, and interpretation [57]. The scope of this study was Cradle-to-Gate, as it encompassed the environmental impact of the four depositions processes utilised considering only the production stage, including the extraction of raw materials (precursors and working gases), and the main inputs and outputs for manufacture (electrical energy for deposition and emissions). The distribution, use, and disposal steps of the life cycle were considered outside of the system's boundary. The LCA technique can also be applied in this type of assessment. The functional unit was the volume of the coating, i.e., coating thickness across the deposition area, in mm<sup>3</sup>.

The environmental impact of manufacturing the coatings was evaluated with SimaPro software (version 9.2.0.2, PRé Sustainability, Amersfoort, The Netherlands) applying the ReCiPe 2016 Endpoint (H) v1.1/World 2010 H/A methodology according to the LCA standards ISO 14040 [57] and ISO 14044 [58]. ReCiPe is a model used to estimate the environmental effects of a product that are connected to a large number of substance emissions and resource extractions. The Hierarchist (H) perspective evaluates the environmental impact with a moderate time horizon of 100 years and only includes substances if there is scientific consensus regarding their effect [59].

With this methodology, the list of the Life Cycle Inventory (amounts of emissions and resource uses) is translated through a sequence of scientifically derived causally related impacts into common units that quantify their damage to different environmental categories across two levels, as illustrated in Figure 3: 18 midpoint characterisation factors which are then converted by a constant mid-to-endpoint factor per impact category into 3 endpoint characterisation factors, i.e., areas of protection, namely damage to human health, damage to ecosystems, and resource scarcity. This characterisation analysis produces scores for each category, providing an overall indication of the environmental impact associated with a product system [59]. All inventory results have been pre-classified to pre-selected impact categories. It should be noted that one substance can contribute to several midpoint impact categories, and likewise, one midpoint category can contribute to multiple endpoint factors [60].



**Figure 3.** The impact categories covered in the ReCiPe2016 method and their relation to the areas of protection [60].

Damage to human health is represented by years lost or whether a person is disabled due to illness or an accident, given in Disability-Adjusted Life Years (DALY). Damage to ecosystems aggregates the local relative species loss in terrestrial, freshwater, and marine ecosystems and is presented as potentially disappeared fractions of species over space and time. Damage to resource availability denotes extra costs (in dollars) involved for future mineral and fossil resource extraction. Normalising the resulting characterisation values for these indicators by dividing each by a set reference value of the average annual impact of a citizen over a period of 1 year resolves the incompatible units, allowing for their direct comparison [60].

# 3. Results and Discussion

#### 3.1. Coating Properties

Table 2 summarises the findings of the coating properties' characterisation. The surface texture and Raman results were averaged from at least three measurements, whilst the nanoindentation tests were conducted over a grid of  $10 \times 10$  indents on each sample.

The mechanical properties of hardness and Young's modulus were set as the point of reference when developing the deposition process in order to ensure that the studied coatings were relevant to the benchmark for each technique. This was verified, since the resulting properties are comparable to what is reported in the literature for undoped DLCs deposited by using the same techniques [24,46,61,62].

Parameters	Unit	dcMS	HiPIMS	PECVD	μW-PECVD
Hardness	[GPa]	$20\pm2$	$44\pm 8$	$23\pm5$	$28\pm2$
Young's modulus	[GPa]	$196\pm14$	$302\pm30$	$191\pm25$	$185\pm9$
H/E	-	$0.102\pm0.014$	$0.154 \pm 0.030$	$0.118 \pm 0.028$	$0.150\pm0.014$
Raman—D peak centre	$[cm^{-1}]$	$1384\pm3$	$1402\pm5$	$1365\pm2$	$1376\pm0$
Raman—G peak centre	$[cm^{-1}]$	$1561\pm4$	$1571\pm1$	$1554\pm0$	$1553\pm1$
Raman—FWHM(D)	$[cm^{-1}]$	$360\pm1$	$362\pm11$	$327\pm4$	$346\pm1$
Raman—FWHM(G)	$[cm^{-1}]$	$174\pm10$	$205\pm3$	$171 \pm 1$	$167\pm3$
$I_D/I_G$	-	$1.22\pm0.02$	$0.69\pm0.04$	$0.42\pm0.03$	$0.44\pm0.06$
RMS roughness, Sq	[nm]	$21\pm 6$	$42\pm12$	$16\pm3$	$15\pm4$
Skewness, Ssk	-	$-10\pm7$	$8\pm4$	$-10\pm10$	$-22\pm12$

Table 2. Characterisation results of DLC coatings for each deposition technique.

### 3.1.1. Atomic Structure

The Raman spectra for all coatings are illustrated in Figure 4. The peak curves were obtained by applying a two-Gaussian fit to the original spectra and averaging the curves of four measurements on different areas of the samples. Finally, the intensities were normalised by using the Standard Normal Variate procedure [63] to facilitate comparison.



**Figure 4.** Normalised Raman spectra of all coatings showing the fitted D and G curve (dashed) and deconvolved D and G peaks (full lines) and corresponding centres: (**a**) dcMS a-C; (**b**) HiPIMS a-C; (**c**) PECVD a-C:H; (**d**) µW-PECVD a-C:H.

Key structural parameters of interest with regards to the local bonding and disorder in DLC coatings can be derived from the Raman spectra, viz., the D and G peaks around 1350 and 1600 cm<sup>-1</sup>, respectively, for visible excitation. On one hand, important information can be ascribed to the ratio between the heights or areas of those peaks, as the higher the value of  $I_D/I_G$  (peak height ratio of D to G curves), the higher the number or the size of

sp<sup>2</sup> clusters present in rings, resulting in a lower crystallinity degree [64]. On the other hand, if the sp<sup>2</sup> phase is predominantly composed of chains, or if the rings are disordered, distorted, or composed of closed chains such that the bonds are not fully delocalized on the rings, then the value of the ratio will be close to zero [65]. Thus, an inverse relationship between this ratio and sp<sup>3</sup> content has been drawn for both a-C and a-C:H [3].

Furthermore, the full-width half-maximum of the G peak, FWHM(G), is sensitive to DLC structure, in that it uniquely corresponds to sp<sup>3</sup> content in H-free DLC [66], although this is not an adequate parameter to calculate the exact sp<sup>3</sup> content; this also holds for a-C:H with a H content under ca. 25 at.% [67]. Another important spectral feature used to interpret the characteristics of DLC is the position of the G peak, as in the three-stage model by Ferrari and Robertson [3], for a-C with an sp<sup>3</sup> fraction higher than 20%, a higher value of the G peak position reveals a higher level of clustering or disorder [3], which is linked to higher sp<sup>3</sup> content [67]. On the other hand, the authors demonstrated that the relation is inverse for a-C:H, i.e., increased sp<sup>3</sup> content is accompanied by a decrease in the G peak position instead.

The main effect of hydrogen in a-C:H is that a higher sp<sup>3</sup> content is achieved mainly by hydrogen saturating the sp<sup>3</sup> sites, rather than by increasing the fraction of C–C bonds. Therefore, at the highest H content, the sp<sup>3</sup> content is highest, wherein the bonding is polymeric and, consequently, the coatings are soft and have a low density; however, at low H contents, sp<sup>2</sup> bonding dominates. In turn, C–C sp<sup>3</sup> bonding is at a maximum, and thus the coatings have the highest density and diamond-like characteristic with an intermediate H content [3].

The higher value of FWHM(G) and the lower value of  $I_D/I_G$  for the a-C deposited by HiPIMS corresponds to a higher content of sp<sup>3</sup> sites, which correlates well with the coating's hardness, i.e., 44 GPa vs. 20 GPa for dcMS a-C. The Raman spectroscopy results are very similar for PECVD a-C:H and  $\mu$ W-PECVD a-C:H, with the resulting hardness of 23 and 28 GPa, respectively, higher than that of dcMS a-C. The presence of a D peak in the a-C:H signals the presence of sp<sup>2</sup> ring clusters; the G peak position around ~1550 cm<sup>-1</sup> points to intermediate levels of the sp<sup>3</sup> fraction [3].

#### 3.1.2. Morphology and Topography

With the exception of HiPIMS a-C, the DLC coatings present a uniform 'cauliflower' surface structure, as is commonly described in the literature [63–65], resulting in low roughness and negative skewness. The SEM image of the HiPIMS a-C in Figure 5 shows a smooth and densely packed bulk surface that is otherwise marred by the presence of defects known as droplets distributed throughout the surface. These droplets were caused by the occurrence of arcing during deposition, which proved difficult to control. In order to obtain the desired mechanical properties, the power parameters employed led to a high peak current, which is a key parameter contributing to the ionization degree of the sputtered species, aiding the formation of sp<sup>3</sup> bonds [68,69], but also induced arcing [68,70], driving the formation of rough carbon droplets on the growing film [71].

This resulted in the surface roughness of the DLC deposited by using HiPIMS being significantly higher than that of the DLCs produced by using the other methods, as well as resulting in a positive value of skewness. Skewness (quotient of the mean cube value of the ordinate values and the cube of root mean square height within a definition area [72]) measures the symmetry of the profile about the mean line, i.e., zero skewness represents a symmetrical height distribution, whilst negative skewness indicates a preponderance of sharp valleys and rounded peaks, and positive skewness indicates more round valleys and sharp peaks [73,74].



**Figure 5.** Secondary electron scanning electron microscope images of the surface morphology of the DLC coatings deposited by using each technique.

It has been reported in the literature [75–77] that higher roughness of DLCs leads to higher friction and wear. Furthermore, Sedlaček et al. [78] found that skewness is the surface texture parameter that most dominantly correlates with friction performance in lubricated contacts, i.e., the more negative it is, the lower the friction. Thus, the poor surface texture quality due to arcing during deposition hinders the potential of HiPIMS a-C as a candidate for energy-efficient tribological performance.

In Figure 6, the cross-sectional morphology of the coatings is shown. a-C deposited by using dcMS has a columnar structure due to limited adatom mobility [79], resulting in a higher deposition rate but lower hardness. A similar columnar structure can be seen in the lower portion of a-C deposited by using HiPIMS, where no bias was initially applied, whereas it is denser on the upper portion of the coating, where substrate bias was applied; notably, the lower structure is nearly as thick as the upper one, as the deposition rate is significantly higher with floating bias due to the densification of the coating provided by biasing the substrate. The a-C:H coatings deposited by using both PECVD and  $\mu$ W-PECVD have similar structures, i.e., they are featureless and densely packed, due to their low ion energy and high ion flux [35]; however, they achieve high deposition rates [80].

#### 3.1.3. Adhesion

Scratch testing is influenced by intrinsic (loading rate, scratch speed, indenter tip radius, wear) and extrinsic factors (mechanical properties of the substrate, coating properties, such as thickness, hardness, modulus, and residual stress, surface roughness, friction between coating and indenter) [81,82]. It is notable in the images.

All coatings suffered the same mode of failure via spallation, which is a ductile failure mode due to buckle propagation and is typical of coatings with high compressive stresses [83], such as DLCs. Evans [84] modelled that the critical buckling stress is proportional to coating thickness squared. Thus, the critical loads (LC1—longitudinal cracks at the borders and chevron cracks on the scratch track, LC2—cracks with local interfacial spallations, and LC3—gross interfacial spallations) reported in Table 3 were also normalised by this parameter by way of comparison, reported between parentheses.



**Figure 6.** Secondary electron SEM images of the cross-sectional morphology of the DLC coatings deposited by using each technique.

**Table 3.** Critical load results of scratch tests, including optical microscope images of one of three scratches performed on each sample.



Both DLCs produced by using the PECVD methods presented nearly equal normalised critical loads, significantly higher than those of both sputtered DLCs, which suggests better abrasive wear resistance of the former two [85]. In fact, all normalised critical loads were lowest for the DLC deposited by using HiPIMS. These results indicate that sputtering

produces coatings with a higher shear modulus, which is inversely correlated with adhesion critical load in hard coatings [86].

These results, however, do not correlate particularly well with the findings of the Rockwell C tests, which causes a different mechanism of failure. Figure 7 shows the imprints of the Rockwell adhesion tests on each coating. HiPIMS a-C, dcMS a-C, and PECVD a-C:H coatings all present small cracks around the entire indentation. However, unlike HiPIMS a-C, which was classified as HF2, both dcMS a-C and PECVD a-C:H coatings also suffered delamination, albeit inextensive, thus classifying them as HF3. In turn,  $\mu$ W-PECVD a-C:H was considered the most inferior, as HF6, due to the large circular delamination seen around the indent, which indicates greater brittleness [85] and thus lower toughness. These results are similar to those reported by Horiuchi et al. [87,88], who also found discrepancies between the adhesion tests due to the different modes of coating failure provoked by the distinct types of loading.



Figure 7. Optical microscope images of the Rockwell C adhesion test imprints on each coating.

#### 3.2. Environmental Impact of Coating Production

Table 4 summarises the results for resource use and yield with regards to the electrical energy utilised and the mass of the respective carbon source material and process gases consumed in one batch. It is worth noting that the electrical energy use comprised all main functions related to coating deposition but not accessory use, such as power for sensors and fans.

In PECVD processes, carbon originates from a precursor gas, acetylene in this case, and thus the consumed mass directly results from flow during deposition. Furthermore, in order to control ion flux and microwave reflective power,  $\mu$ W-PECVD requires the use of Ar mixed with acetylene. Excess acetylene is then rejected into the atmosphere, diluted with nitrogen due to its risk of exploding (the discarded amount of acetylene was considered equal to the consumed amount, given the deposited mass is negligible).

On the other hand, in the case of sputtering, a graphite target is bombarded by a working gas (Ar here) and releases carbon neutrals and ions for deposition. Every sputtering target has a lifetime that is determined by the energy supplied to it and is limited to a maximum erosion depth up to which the target remains functional. Once the target reaches this erosion limit, it is usually disposed of (a graphite target is unlikely to be recycled). For this reason, the carbon mass consumed for the sputtering processes indicated in Table 4 is not simply the sputtered mass that is eroded from the target but also comprised the equivalent mass of the target in relation to its total mass and consumed lifetime.

Parameters	Unit	dcMS	HiPIMS	PECVD	μW-PECVD
DLC thickness	[µm]	1.49	1.72	0.83	0.90
DLC deposition rate	[nm/min]	16.6	9.6	9.2	15
Available deposition area	[mm <sup>2</sup> ]	$2.7 imes10^5$		$9.0  imes 10^5$	
Output rate (total time)	[nm.m <sup>2</sup> /min]	1.5	1.3	2.6	2.7
Source of DLC	-	graphite		C <sub>2</sub> H <sub>2</sub>	
DLC source consumption	[g]	3.6, eq.	12.1, eq.	27.8	14.2
Average C source consumption—DLC	$[mg/(\mu m.mm^2)]$	0.0090	0.026	0.037	0.017
Average C consumption—interlayer	$[mg/(\mu m.mm^2)]$	0.0018	0.0015	0.0010	-
Average Cr consumption—interlayer	$[mg/(\mu m.mm^2)]$	0.015	0.013	0.0082	0.0075
Average WC consumption—interlayer	$[mg/(\mu m.mm^2)]$	-	-	-	0.019
Average Ar consumption	$[mg/(\mu m.mm^2)]$	0.113	0.258	0.029	0.075
Average N <sub>2</sub> consumption	$[mg/(\mu m.mm^2)]$	-	-	1.49	1.59
	En	ergy use			
Heating	[kJ]	28,037	0	34,193	35,662
Target cleaning + plasma etching	[kJ]	25,610	25,610	25,610	25,610
Interlayer	[kJ]	11,786	11,745	11,794	20,284
DLC	[kJ]	15,977	99,233	2,682	15,576
Pumping	[kJ]	111,660	152,580	122,160	124,260
Average energy use	$[J/(\mu m.mm^2)]$	480	623	263	273

Table 4. Resources consumed in one batch and resulting DLC thickness for each deposition technique.

For illustration purposes, in the case of the graphite target, which weighs 2040 g, the maximum energy input through its lifetime is  $9 \times 10^6$  kJ according to the manufacturer. During the carbon deposition step, 15,977 kJ and 53,532 kJ of energy were applied to the cathode by means of dcMS and HiPIMS, respectively, which corresponds to 0.18% and 0.59% of the cathode's lifetime. Thus, an equivalent of 3.6 g and 12.1 g of the graphite target was consumed to deposit the a-C. The same calculation was used for the other sputtering steps, i.e., for the interlayer of all coatings. The maximum energy input of the Cr and WC targets was also  $9 \times 10^6$  kJ.

Furthermore, it is important to consider how the differing sources of carbon may affect the environmental impact of the coatings. In the sputtering processes, the solid graphite target used is innocuous to the environment, while the reactive PECVD method requires a chemical vapour precursor species. Various hydrocarbons, with varying carbon footprints, can be used for DLC production, which could affect the deposition rate [38], although density and hardness remain unaffected [20]. This work used acetylene as the PECVD carbon precursor, which has null Global Warming Potential (GWP, a measure of how much energy the emission of 1 ton of a gas will absorb over a given period of time—typically 100 years—relative to the emission of 1 ton of  $CO_2$  [89]); in contrast, butane, e.g., would have a higher deposition rate, but its total GWP is reportedly 3–6.5 [90,91]. Moreover, acetylene presents no health or environmental hazard as an air pollutant [92]; therefore, it can be regarded as an eco-friendly precursor choice. Ultimately, multiple aspects that drive the environmental impact of elements are reflected in an LCA.

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Another important matter that must be factored into the environmental impact calculation is the deposition output rate. One caveat of sputtering is that it is highly dependent on the line of sight of the ions sputtered from the target, so much so that the obtained deposition rates of both dcMS and HiPIMS—comparable to those of  $\mu$ W-PECVD and PECVD, respectively—were only enabled by keeping the substrates stationary in front of the target. Previous experimentation by the authors showed that applying table rotation could potentially halve the deposition rate. Meanwhile, as PECVD uses a gaseous precursor, the substrates are allowed 2-fold rotation, i.e., not only does the substrate table rotate, but the spindles that the substrates are fixed to also spin themselves. This leads to higher deposition rates while facilitating coating uniformity over complex geometries.

Consequently, it is important to concede that each deposition batch created by using dcMS and HiPIMS has a significantly lower areal output compared to using PECVD and  $\mu$ W-PECVD. This will be taken into account when calculating resource consumption by averaging the total energy and precursor use by thickness and the available deposition area, which is estimated based on chamber geometry (as presented on the last row of Table 4, in J/( $\mu$ m.mm<sup>2</sup>)). Thickness uniformity throughout the deposition area is assumed for this work.

The power used by each factor, such as heating, bias, cathode, coils (power source for PECVD), microwave source, and anode (for substrate plasma etching), was directly monitored on the computer that controls deposition. The heater has a maximum power of 36 kW. A maximum cathode power of 3 kW and a current of 5 A on each of the four coils were applied during target cleaning, as per themethod. Plasma etching was generated by using a maximum anode current of 60 A and a supplementary power supply. Since small variations occur in every batch, these steps are not unique to any process, so the highest value obtained was adopted for all four techniques: 8150 kJ for target cleaning, plus 17,460 kJ for plasma etching. Maximum power was assumed for the roughing pump (6.9 kW) at all times and for the turbomolecular pump (200 W) during base pumping, and then minimum power (100 W) was considered for the turbo pump during the other steps, given that the pressure is significantly higher than the ultimate pressure. The energy used during the deposition steps comprised bias power, cathode power where applicable, and coil or microwave power for the PECVD processes, as per the method.

Figure 8 shows the characterisation and normalised results of the environmental profiles of manufacturing 1 mm<sup>3</sup> of each coating, categorised in the three endpoint areas of protection, which represent the sum of the midpoint areas considered in the methodology used, as seen in Figure 3. Characterisation directly quantifies the environmental impact of the resources consumed in the three endpoint categories: human health, which includes toxicity, respiratory, and carcinogenic issues, due to exposure to harmful chemicals and pollutants; ecosystem health, including global warming, loss of biodiversity, and habitat degradation; and depletion of natural resources.

As can be seen in Figure 8, the manufacturing of 1 mm<sup>3</sup> of the DLC coatings causes a loss of approximately  $1 \times 10^{-7}$  Disability-Adjusted Life Years among humans, the disappearance of  $1 \times 10^{-7}$  species over a year, and USD  $5 \times 10^{-3}$  of extra costs for future resource extraction. In all categories, PECVD is the deposition technique with the lowest environmental impact, closely followed by  $\mu$ W-PECVD, whilst HiPIMS resulted in the highest impact—~130% higher than PECVD a-C:H across all three endpoint impact categories. This is explained by a significantly greater share being attributed to the electricity used for all techniques.



**Figure 8.** A comparison of the environmental impact of manufacturing 1 mm<sup>3</sup> of DLC by using the four studied processes (endpoint characterisation and normalisation results sorted by damage category; log-10 scale).

Normalisation is carried out by dividing each characterised impact score by the total impact in a reference system—in this case, the global impact in a given year—and thus it is dimensionless. Its primary purpose is to contextualise and facilitate interpretation of the results by expressing the different impact indicator scores on a common scale, which

supports comparisons across impact categories and allows for the identification of the most relevant impacts [59]. The normalisation results show that the most damage is caused to human health; this is due to the impact on global warming as a result of electricity use.

It is important to note that the greatest energy consumption share throughout the process originated in the pumping stage, which is directly related to deposition time and thus to deposition rate. Whilst a higher deposition rate has been reported for  $\mu$ W-PECVD a-C:H [34], its need for a thicker interlayer and the inherent higher energy of the plasma source lead to greater energy use compared to PECVD. Meanwhile, not only is HiPIMS a more energy-intensive process in itself, but its low ionization rate leads to a long deposition process, even after limiting the areal output. Therefore, improving deposition rates is the key factor to reducing the environmental impact of DLC deposition.

#### 4. Conclusions

This work utilised the power of LCA to evaluate the environmental impact of different technologies for manufacturing DLC coatings.

The  $\mu$ W-PECVD process had the highest output rate, which considers not only the coating deposition rate but also the product areal yield possible for each process. PECVD expended the lowest energy per output; meanwhile, HiPIMS had the lowest output rate whilst consuming the highest amount of energy, i.e., it is the least energy-efficient process. In turn, PECVD required the most amount of carbon, whereas dcMS used the least, but both source materials are innocuous to the environment and human health. Ultimately, the LCA demonstrated that electrical energy use, as dictated by deposition rate, was by far the most significant factor contributing to the environmental impact of all deposition rates are the key factor to lowering the environmental impact of DLC coating manufacturing.

Furthermore, the surface quality of HiPIMS a-C was adversely affected by excessive arcing during deposition, causing greater roughness and a preponderance of peaks in the morphology. Whilst higher-frequency magnetron sputtering was developed to suppress the arcing problem [93], especially in comparison to the traditional Cathodic Arc Deposition method, arcing can still occur with HiPIMS [94], depending upon parameters such as current levels and target quality [95]. HiPIMS deposition in this work used an old generation power supply that struggled with arcing issues; moreover, the power parameters applied in order to achieve high-hardness DLC led to high current levels, which also contributed to significant arcing. In turn, both PECVD and  $\mu$ W-PECVD processes produced the smoothest coatings.

Adhesion as determined by scratch testing was very similar for both sputtered a-C samples and was not too inferior compared to PECVD a-C:H, but  $\mu$ W-PECVD a-C:H failed at significantly higher critical loads. The results of the Raman spectroscopy analysis point to an increased ratio of sp3 bonds in HiPIMS a-C. This is reflected in the fact that the measured value of hardness of HiPIMS a-C is approximately twice the value of the other coatings. Moreover, HiPIMS a-C also has the highest value of H/E, although that of  $\mu$ W-PECVD a-C:H is comparable.

Based on the results of the four presented techniques,  $\mu$ W-PECVD could be considered the 'greenest' production method of DLC for tribology due to its low environmental impact per output whilst obtaining a high H/E ratio with good scratch adhesion, resulting in good wear resistance. In the future, an assessment of the tribological performance of these coatings can be implemented into the LCA, including their use phase, in addition to manufacturing in order to evaluate their overall life cycle environmental impact. **Author Contributions:** Conceptualization, L.I., A.C., A.M., and L.Y.; methodology, L.I.; validation, G.W.; formal analysis, L.I.; investigation, L.I.; data curation, L.I.; writing—original draft preparation, L.I.; writing—review and editing, G.W., A.C., A.M., and L.Y.; supervision, A.C., A.M., and L.Y.; funding acquisition, A.M. All authors have read and agreed to the published version of the manuscript.

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# Abbreviations

The following abbreviations are used in this manuscript:

DALY	Disability-adjusted life years
dcMS	Direct current magnetron sputtering
DLC	Diamond-like carbon
FWHM	Full-width half-maximum
HiPIMS	High-power impulse magnetron sputtering
LCA	Life cycle analysis
MS	Magnetron sputtering
PECVD	Plasma-enhanced chemical vapour deposition
SEM	Scanning electron microscopy
μW-PECVD	Microwave plasma-enhanced chemical vapour deposition

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