

The Influence of Plasma-Assisted Production and Milling Processes of DLC Flakes on Their Size, Composition and Chemical Structure

Tomasz Kaźmierczak, Piotr Niedzielski and Witold Kaczorowski *

Faculty of Mechanical Engineering, Institute of Material Sciences and Engineering, Lodz University of Technology, Stefanowskiego 1/15, 94-924 Lodz, Poland

Abstract: Diamond-like carbon (DLC) flakes were produced using a dual-frequency method: microwave/radiofrequency plasma-assisted chemical vapour deposition (MW/RF PACVD) with the use of methane or its mixture with gases such as hydrogen, argon, oxygen or nitrogen. Their modification was performed using a planetary ball mill with and without a fluid: deionised water or methanol. Changes occurring in the morphology of flake surfaces were presented in pictures taken using a scanning electron microscope (SEM). Their composition and chemical structure were analysed using Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The presented research results show that it is possible to control the size of flakes and their chemical structure. An increase in the C-C sp^3 bond content in produced carbon-based materials is only possible by modifying DLC flakes during their production process by introducing oxygen or argon into the working chamber together with the carbon-carrying gas. In the processes of mechanical DLC flake modification, it is necessary to add fluid to limit the occurrence of graphitisation processes. The research conducted shows that methanol is best used for this purpose as its use results in a decrease in the percentage of C-C sp^3 bonds as compared to the materials, before milling, of only 1.7%. A frequent problem both in the production of DLC flakes and during their mechanical modification is the introduction of additional elements into their structure. Admixing electrode materials from the plasma-chemical device (iron) or grinding beads (zirconium) to DLC flakes was observed in our studies. These processes can be limited by the appropriate selection of production conditions or by mechanical modifications.

Keywords: diamond-like carbon; flakes; plasma; milling; Raman spectroscopy

Introduction

Carbon materials in a fragmented or thin-layered form are the basis for numerous contemporary studies and applications. The largest number of studies in this area, as presented in the global literature, pertain to powders in the form of nanotubes, graphene or nanodiamonds [1–3]. Excellent methods for their production, cleaning and functionalisation are known [4–7]. This, however, does not change the fact that this area is still valid and numerous researchers continue their studies on other forms of carbon, including diamond-like carbon (DLC). DLC is excellent as a low-friction or anti-wear coating [8,9] especially in medical applications [10,11] and it is often modified by adding various elements, e.g., Si, Ag, F or Ti [12–14]. It can also be used for the production of carbon-based fragmented materials, which are usually described in the literature as flakes or powders [15,16]. The name of DLC covers many types of materials which are mostly a mixture of C-C sp^3 and C=C sp^2 bonds and also hydrogen [17,18].

Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) are usually used to identify these materials. The former allows qualitative determination of the chemical structure, in particular, the presence of characteristic bonds between carbon atoms as well as carbon and hydrogen. The obtained spectra, after deconvolution, are helpful in the specification of the ID/IG ratio, whose change may directly indicate changes in the number of C-C sp^3 bonds in DLC. The other technique, i.e., XPS, allows a quantitative evaluation of both chemical composition and chemical structure of carbon materials.

Carbon powders, especially DLC flakes, are a very interesting material for numerous applications. We can find them, amongst other things, as an element of composites [15], material for biomedical applications [16,19,20], or in light-emitting diodes [21]. On the one hand, their use as a polymer matrix filler can improve the mechanical and tribological properties of composites. On the

other hand, they are an interesting model material for examining the biological properties of carbon coatings. A number of reports can be found in the literature related to their impact on the cellular level, which show their low toxicity [16,22]. Like the coatings, DLC flakes or powders can also be susceptible to doping of various elements and compounds (e.g., carbon quantum dots), which makes them an excellent material for fabrication of high-efficiency LEDs [20]. DLC flakes can be obtained using many methods (e.g., microwave-assisted pyrolysis); however, they are much more often produced in the form of delaminated carbon coating. The latter method uses the phenomenon of coating cracking when the maximum internal stress levels are exceeded. This effect can be enhanced by using a base with the coefficient of thermal expansion divergent from the coefficient of thermal expansion of DLC coating e.g., an aluminium base (as in Ohana et al. study [15]). In this type of research, processes based on chemical vapour deposition (CVD) methods are usually used; in particular, ones which use radio, dual-frequency activated plasma microwave/radiofrequency (MW/RF), DC or pulsed-bias voltage and a methane, acetylene or toluene atmosphere [19–22]. Additionally, the number of carbon powders formed in CVD plasma can be determined by the selection of an appropriate working atmosphere e.g., the largest quantities are created when a large amount of hydrogen is introduced into the reactor in relation to the carbon-carrying gas [21]. However, DLC flakes acquired using CVD methods are usually characterised by a broad range of sizes. Attempts are made to reduce this range by additional mechanical processing—milling [23]. Additionally, milling offers a lot of opportunities to acquire and dope carbon materials, including nanomaterials.

It would appear that the area of DLC flake use produced by CVD methods could be extended if research performed in this area led to the formation of materials characterised by appropriate purity and uniform size. The aspects listed above are particularly important for biological research conducted on DLC flakes in which all changes in the chemical and phase composition influence the results obtained. Unfortunately, the most popular methods of DLC flake acquisition involve the risk of elements from electrode or modified media (during production processes) or utensil and bead materials (during milling processes) becoming spontaneously doped to the flakes [23]. The presented problems are the basis of the research conducted and presented in this publication.

Materials and Methods

Diamond-Like Carbon Flakes Deposition Process

DLC flakes were produced using a device based on the MW/RF plasma-assisted chemical vapour deposition (PACVD) method which was described in earlier publications [16,19,23]. This technique combines the advantages of microwave (2.45 GHz) and radio frequency plasma (13.56 MHz), allowing the control of degree of ionisation of the working atmosphere and the level of ion energy using RF bias [8,24]. The conducted work shows that, using this method, the deposition rate of the DLC coatings can be varied from 1 to 18 m/h, which is close to the growth rate of carbon nanowalls [25]. Preliminary research on the possibility of producing DLC flakes using MW/RF plasma was conducted using methane and its mixtures with hydrogen, argon, oxygen and nitrogen and time of 120 min, in accordance with the parameters presented in Table 1. All the carbon flakes were deposited at RF and MW forwarded power equal to 500 W, under the negative self-bias of 500 V. The processes have proven that it is possible to produce delaminated DLC coatings on water-cooled RF electrodes and have shown, at the same time, the influence of gases introduced into the working chamber on the morphology, composition and chemical structure of powders obtained. All processes were implemented using the same energy conditions at a pressure ranging from 100 to 130 Pa. For milling processes, carbon flakes were produced in a pure methane atmosphere over a 200-min period. After finishing of plasmachemical processes, flakes were collected with a brush from the electrode.

Table 1. Parameters of carbon powder production processes.

RF Power	MW Power	Gas Flow [sccm]					Pressure	Time of
[W]	[W]	CH ₄	H ₂	Ar	O ₂	N ₂	[Pa]	Deposition [min]
			-	-	-	-		120–200
			20	-	-	-		120
500	500	180	-	20	-	-	100–130	120
			-	-	20	-		120
			-	-	-	20		120

Milling Process

Mechanical powder modification was conducted using a PM100 (Retsch GmbH, Haan, Germany) planetary ball mill. The milling was performed in a zirconium oxide (ZrO₂) dish with a capacity of mL using ZrO₂ beads with a diameter of 1 mm. Each time, these processes were performed using the 20:1 bead weight to DLC flake ratio. The applied speed of the mill ranged from 300 to 600 rpm and the milling process duration was 10 h. Fluid in the form of deionised water or methanol (10 mL) was added to the dish (or not). All of the parameters of milling processes were selected on the basis of calculations performed using the Taguchi method [23].

Surface Characterisation

The morphology of the DLC flakes produced was analysed using Scanning Electron Microscopy SEM (Hitachi S-3000N, Kyoto, Japan). Increments of materials produced in CVD processes were selected so as to allow for comparisons between the processes. SEM images, after milling processes, were enlarged so as to allow an analysis of the sizes obtained after mechanical processing.

The composition and chemical structure were analysed using X-ray photoelectron spectroscopy (XPS). In this part of the study, the ESCALAB-210 system (VG Scientific, Fison, Glasgow, UK)—equipped with a non-monochromatic Al source (K_α = 1486.6 eV) operating at 14.5 kV and 20 mA—was used. For the tested DLC flakes, the C1s peak calibration was performed for the peak position amounting to 284.6 eV [26,27]. To obtain a more accurate analysis, the C1s peak was adapted using Gauss–Lorentz curves corresponding to sp² C-C, sp³ C=C and C-N, C-O, C=O bonds, which maximum values equal to approximately 284.5 eV, 285.3 eV, 285.93 eV, 286.1 eV and 288 eV, respectively [27,28]. Additionally, the chemical structure of the powders produced was analysed using Confocal Raman Spectroscopy, the inVia device (Renishaw plc, Gloucestershire, UK), operating at a wavelength of 532 nm. These tests were performed with a spectral resolution of 1 cm⁻¹ at a range from 1000 to 1800 cm⁻¹. The exposure time was 200 s. The obtained spectra were deconvoluted using a two-peak model with Peakfit software v.4.12.

Results and Discussion

DLC Flakes Produced Using the MW/RF PACVD Method

SEM pictures of the flakes produced in this part of the study are presented in Figure 1. The presented carbon materials were produced on the steel surface of an RF electrode using processes conducted in a methane atmosphere or its mixture with hydrogen, argon, oxygen and nitrogen (in accordance with Table 1). It can be seen in the pictures that the presence of oxygen and argon promotes. SEM pictures of the flakes produced in this part of the study are presented in Figure 1. The presented carbon materials were produced on the steel surface of an RF electrode using processes conducted in a methane atmosphere or its mixture with hydrogen, argon, oxygen and nitrogen (in accordance with Table 1). It can be seen in the pictures that the presence of oxygen and argon the reduction of thickness and the size of the powders produced, probably due to the intensification of promotes the reduction of thickness and the size of the powders produced, probably due to the etching processes (Figure 2c,d). DLC flakes produced in an atmosphere of

methane, methane with intensification of etching processes (Figure 2c,d). DLC flakes produced in an atmosphere of methane, nitrogen or hydrogen have a shape of thick pieces of carbon coating detached from the electrode methane with nitrogen or hydrogen have a shape of thick pieces of carbon coating detached from the (Figure 2a,b,e). On the basis of the presented pictures, it can be established that the flakes produced in electrode (Figure 2a,b,e). On the basis of the presented pictures, it can be established that the flakes the methane plasma, or with the addition of hydrogen, have an average size of approximately 50 m. produced in the methane plasma, or with the addition of hydrogen, have an average size of When argon and oxygen were used as the additional gas, these parameters were reduced to 35 m (for approximately 50 μm . When argon and oxygen were used as the additional gas, these parameters argon) \sim 25 m (for oxygen). Flakes produced in the methane-nitrogen plasma, on the other hand, had were reduced to 35 μm (for argon) \sim 25 μm (for oxygen). Flakes produced in the methane-nitrogen a size of over 80 m.

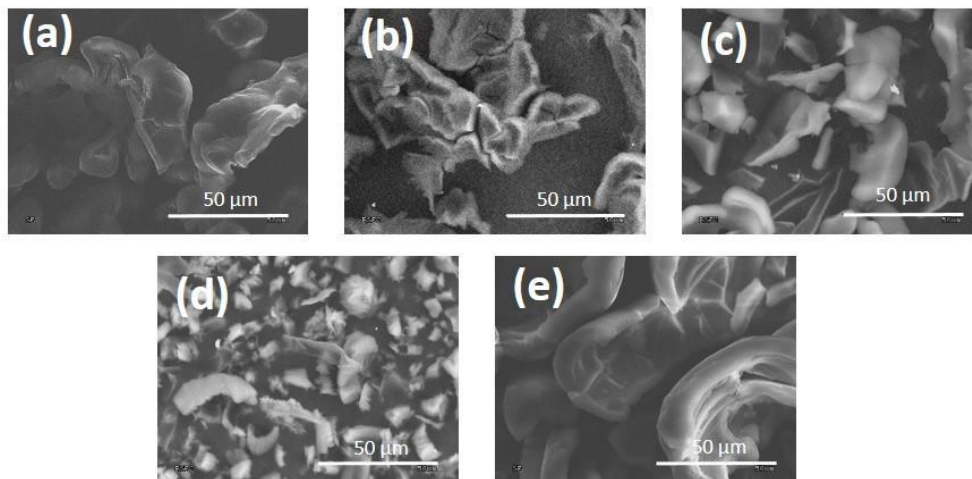


Figure 1. Powder produced using (a) methane; (b) methane and hydrogen mixture; (c) methane and argon mixture; (d) methane and oxygen mixture; and (e) (methane) and nitrogen mixture.

Further analysis of the obtained carbon materials was conducted using Raman spectroscopy and XPS. Raman spectra of the DLC flakes produced are presented in Figure 2 and Table 2 contains a detailed analysis of them. It can be seen that a change of the gas mixture used in DLC flake production processes influences the obtained ID/IG ratio, which is closely correlated to the content of C-C sp³ bonds in produced flakes. The material obtained in the process conducted in the methane-oxygen atmosphere was characterised by a lowest ratio of 0.46, while the highest ID/IG parameters (2.64) were obtained for processes in the methane-nitrogen atmosphere. By analysing the parameters collected in Table 2, it can be concluded that powders produced with the use of methane-nitrogen plasma are graphite-like. The observed decrease in full width at half maximum of the G peak, together with an increase in its position value, is typical of graphite-like carbon materials (GLC) [29]. In case of other samples deposited by MW/RF PACVD method, the described parameters change is consistent with the changes in the ID/IG ratio.

XPS technique (VG Sci. ESCALAB-210, Fison, Glasgow, UK). The obtained structure and chemical composition of tested materials is presented in Table 3. The presented results were obtained by means of a characteristic peak analysis describing the C1 peak, as shown in Figure 3.

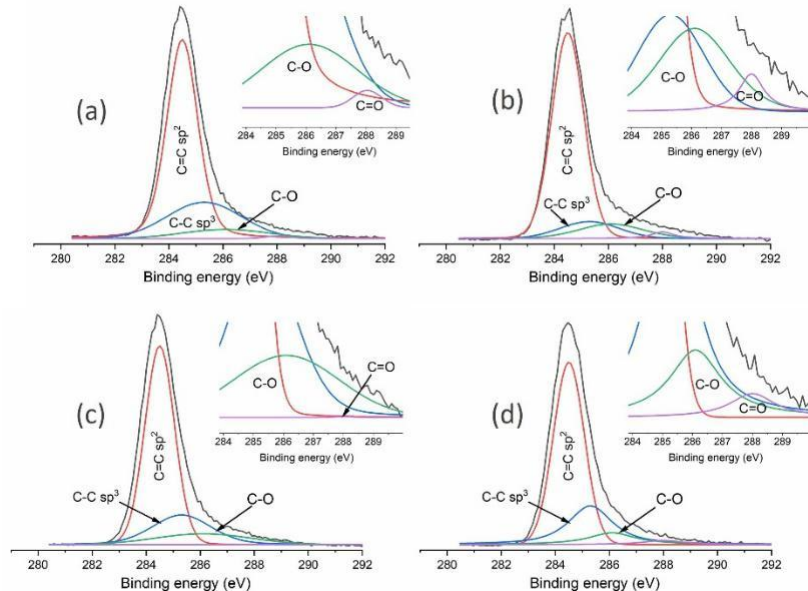


Figure 6. Analysis of C1s peaks obtained in XPS tests of powders produced using (a) the CVD method; (b) dry-milled; (c) milled in water; (d) milled in methanol.

Conclusions

This study presents the most important aspects of DLC flake production using the MW/RF PACVD method. The use of this method involves the risk of introducing additional elements from electrodes or media into the structure. However, this problem can be solved using longer processes of DLC electrodes or media into the structure. However, this problem can be solved using longer processes flake production. At this stage of powder production, the chemical structure of a powder can also be controlled, for example, by the selection of a gas mixture added to these processes (such as in this study). However, one needs to be aware that the use of gases which allow for quicker etching of C-C bonds will involve a decrease in the efficiency of such processes. The addition of oxygen to the methane atmosphere had the greatest effect on the C-C sp³/(C-C sp³ + C-C sp²) ratio. It resulted in an increase in the content of C-C sp³ bonds in DLC flakes—from 24.3% to 28.8%. This effect is typical of the production of DLC coatings where the use of oxygen promotes the formation of C-C sp³ and etching of the C-C sp² bonds at the same time. A similar analogy for DLC coatings can be observed in the etching of the C-C sp² bonds at the same time. A similar analogy for DLC coatings can be observed in studies using nitrogen and hydrogen whose addition can promote graphitisation of carbon materials. This can be clearly seen for nitrogen where the results obtained indicate a GLC structure. Additionally, the parameters of plasma-based processes influence the

size of the flakes obtained. With the use of Additionally, the parameters of plasma-based processes influence the size of the flakes obtained. oxygen and argon as an additional gas introduced in the process (together with methane), sizes of With the use of oxygen and argon as an additional gas introduced in the process (together with approximately 25 and 35 m were obtained respectively, i.e., approximately half less than for powders ethane), sizes of approximately 25 and 35 μm were obtained respectively, i.e., approximately half produced under different conditions. Less than for powders produced under different conditions.

When using the DLC flake milling process, one needs to remember, that just like in the production, When using the DLC flake milling process, one needs to remember, that just like in the about both the effect of introducing additional elements into the structure (Zr in the presented case) production, about both the effect of introducing additional elements into the structure (Zr in the which come from dish walls and milling beads and the biggest hazard—the graphitisation of materials.

Presented case which come from dish walls and milling beads and the biggest hazard—the Such mechanical processing causes an increase in the temperature which leads to the conversion of graphitisation³ of materials². Such mechanical processing causes an increase in the temperature which sp bonds into sp . It is possible to limit this phenomenon by using fluid, which acts as an agent leads to the conversion of sp³ bonds into sp². It is possible to limit this phenomenon by using fluid, which reduces friction and takes away excess temperature from the system into the dish. It has been which acts as an agent which reduces friction and takes away excess temperature from the 3system determined that the dry-milling processes cause a drastic decrease in the percentage of C-C sp bonds into the dish. It has been determined that the dry -milling processes cause a drastic decrease in the from approximately 26% (for the powder before milling) to 11%. In this case, an increase in the percentage of C-C² sp³ bonds from approximately 26% (for the powder before milling) to 11%. In this percentage of sp bonds is additionally observed (from 66.1% to 75.2%) and in carbon with oxygen. case, an increase in the percentage of sp² bonds is additionally observed (from 66.1% to 75.2%) and An analysis of the results for powders milled in water and in methanol makes it possible to establish

in carbon with oxygen. An analysis of the results for powders milled in water and in methanol makes that the fluids used can limit graphitisation processes which occur for dry milling. Methanol is the it possible to establish that the fluids used can limit graphitisation processes which occur for dry milling. Methanol is the best in this respect as its use resulted in a decrease in the percentage of C-C sp³ bonds as compared to the materials before milling of only 1.7%. Additionally, an interesting result best in this respect as its use resulted in a decrease in the percentage of C-C sp³ bonds as compared to the materials before milling of only 1.7%. Additionally, an interesting result is the possibility of limiting the degree of pollution of produced carbon products by using water in the milling process. The presented results can be used for developing combined DLC flake production technologies with a strictly specified structure and chemical composition and high uniformity in size.

Author Contributions: Conceptualization, W.K.; methodology, T.K. and W.K.; validation, P.N., T.K. and W.K.; formal analysis, W.K and P.N.; investigation, T.K. and W.K.; resources, W.K.; data curation, W.K.; writing—original draft preparation, W.K.; writing—review and editing, W.K. and P.N.; visualization, W.K.; supervision, P.N.; All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: All of the work was carried out in the Institute of Material Sciences and Engineering of the Lodz University of Technology.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1) Salvo-Comino, C.; Rassas, I.; Minot, S.; Bessueille, F.; Arab, M.; Chevallier, V.; Rodriguez-Mendez, M.L.; Errachid, A.; Ja rezic-Renault, N. Voltammetric Sensor Based on Molecularly Imprinted Chitosan-Carbon Nanotubes Decorated with Gold Nanoparticles Nanocomposite Deposited on Boron-Doped Diamond Electrodes for Catechol Detection. *Materials* **2020**, *13*, 688. [[CrossRef](#)]
- 2) Lu, X.; Liang, B.; Sheng, X.; Yuan, T.; Qu, J. Enhanced thermal conductivity of polyurethane/wood powder composite phase change materials via incorporating low loading of graphene oxide nanosheets for solar thermal energy storage. *Sol. Energy Mater. Sol. Cells* **2020**, *208*, 110391. [[CrossRef](#)]
- 3) Kume, A.; Mochalin, V.N. Sonication-assisted hydrolysis of ozone oxidized detonation nanodiamond. *Diam. Relat. Mater.* **2020**, *103*, 107705. [[CrossRef](#)]
- 4) Shah, K.A.; Tali, B.A. Synthesis of carbon nanotubes by catalytic chemical vapour deposition: A review on carbon sources, catalysts and substrates. *Mater. Sci. Semicond. Process.* **2016**, *41*, 67–82. [[CrossRef](#)]
- 5) Xu, J.; Cao, Z.; Zhang, Y.; Yuan, Z.; Lou, Z.; Xu, X.; Wang, X. A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: Preparation, application, and mechanism. *Chemosphere* **2018**, *195*, 351–364. [[CrossRef](#)]
- 6) Zhang, Y.; Rhee, K.Y.; Hui, D.; Park, S.J. A critical review of nanodiamond based nanocomposites: Synthesis, properties and applications. *Compos. Part B Eng.* **2018**, *143*, 19–27. [[CrossRef](#)]
- 7) Edgington, R.; Spillane, K.M.; Papageorgiou, G.; Wray, W.; Ishiwata, H.; Labarca, M.; Leal-Ortiz, S.; Reid, G.; Webb, M.; Foord, J.; et al. Functionalisation of Detonation Nanodiamond for Monodispersed, Soluble DNA-Nanodiamond Conjugates Using Mixed Silane Bead-Assisted Sonication Disintegration. *Sci. Rep.* **2018**, *8*, 728. [[CrossRef](#)] [[PubMed](#)]
- 8) Kaczorowski, W.; Szymanski, W.; Batory, D.; Niedzieski, P. Tribological Properties and Characterization of Diamond like Carbon Coatings Deposited by MW/RF and RF Plasma-Enhanced CVD Method on Poly (ether-ether-ketone). *Plasma Process. Polym.* **2014**, *11*, 878–887. [[CrossRef](#)]
- 9) García, J.A.; Rivero, P.J.; Barba, E.; Fernández, I.; Santiago, J.A.; Palacio, J.F.; Fuente, G.G.; Rodríguez, R.J. A Comparative Study in the Tribological Behavior of DLC Coatings Deposited by HiPIMS Technology with Positive Pulses. *Metals* **2020**, *10*, 174. [[CrossRef](#)]
- 10) Choudhury, D.; Morita, T.; Sawae, Y.; Lackner, J.M.; Towler, M.; Krupka, I. A novel functional layered diamond like carbon coating for orthopedics applications. *Daim. Relat. Mater.* **2016**, *61*, 56–69. [[CrossRef](#)]
- 11) Liao, T.T.; Zhang, T.F.; Li, S.S.; Deng, Q.Y.; Wu, B.J.; Zhang, Y.Z.; Zhou, Y.J.; Guo, Y.B.; Leng, Y.X.; Huang, N. Biological responses of diamond-like carbon (DLC) films with different structures in biomedical application. *Mater. Sci. Eng. C* **2016**, *69*, 751–759. [[CrossRef](#)] [[PubMed](#)]
- 12) Bouabibsa, I.; Lamri, S.; Sanchette, F. Structure, Mechanical and Tribological Properties of Me-Doped Diamond-Like Carbon (DLC) (Me = Al, Ti, or Nb) Hydrogenated Amorphous Carbon Coatings. *Coatings* **2018**, *8*, 370. [[CrossRef](#)]
- 13) Batory, D.; Jedrzejczak, A.; Kaczorowski, W.; Kolodziejczyk, L.; Burnat, B. The effect of Si incorporation on the corrosion resistance of a-C:H:SiOx coatings. *Daim. Relat. Mater.* **2016**, *67*, 1–7. [[CrossRef](#)]
- 14) Mazare, A.; Anghel, A.; Surdu-Bob, C.; Totea, G.; Demetrescu, I.; Ionita, D. Silver doped diamond-like carbon antibacterial and corrosion resistance coatings on titanium. *Thin Solid Films* **2018**, *657*, 16–23. [[CrossRef](#)]
- 15) Ohana, T.; Nakamura, T.; Tanaka, A. Tribological properties of polymer composites with diamond-like carbon flakes. *Daim. Relat. Mater.* **2010**, *19*, 894–898. [[CrossRef](#)]
- 16) Solarska, K.; Gajewska, A.; Kaczorowski, W.; Bartosz, G.; Mitura, K. Effect of nanodiamond powders on the viability and production of reactive oxygen and nitrogen species by human endothelial cells. *Daim. Relat. Mater.* **2012**, *21*, 107–113. [[CrossRef](#)]
- 17) Grill, A. Diamond-like carbon: State of the art. *Daim. Relat. Mater.* **1999**, *8*, 428–434. [[CrossRef](#)]
- 18) Grill, A. Plasma-deposited diamondlike carbon and related materials. *IBM J. Res. Dev.* **1999**, *43*, 147–162. [[CrossRef](#)]

- 19) Batory, M.; Batory, D.; Grabarczyk, J.; Kaczorowski, W.; Kupcewicz, B.; Mitura, K.; Nasti, T.H.; Yusuf, N.; Niedzielski, P. Biological properties of carbon powders synthesized using CVD and detonation methods. *J. Nanosci. Nanotechnol.* **2012**, *12*, 9037–9046. [[CrossRef](#)]
- 20) Li, H.; Zhang, Z.; Ding, J.; Xu, Y.; Chen, G.; Liu, J.; Zhao, L.; Huang, N.; He, Z.; Li, Y.; et al. Diamond-like carbon structure-doped carbon dots: A new class of self-quenching-resistant solid-state fluorescence materials toward light-emitting diodes. *Carbon* **2019**, *149*, 342–349. [[CrossRef](#)]
- 21) Lin, H.C.; Yu, J.F.; Shiue, S.T.; Lin, H.Y. Characteristics of carbon coatings on optical fibers prepared by radio-frequency plasma enhanced chemical vapor deposition with different H₂/C₂H₂ ratios. *Thin Solid Films* **2010**, *518*, 7492–7496. [[CrossRef](#)]
- 22) Bakowicz-Mitura, K.; Bartosz, G.; Mitura, S. Influence of diamond powder particles on human gene expression. *Surf. Coat. Technol.* **2007**, *201*, 6131–6135. [[CrossRef](#)]
- 23) Kazimierczak, T.; Kaczorowski, W.; Niedzielski, P. CVD carbon powders modified by ball milling. *Mater. Sci.-Poland* **2015**, *33*, 521–528. [[CrossRef](#)]
- 24) Kaczorowski, W.; Niedzielski, P. Morphology and Growth Process of Carbon Films Prepared by Microwave / Radio Frequency Plasma Assisted CVD. *Adv. Eng. Mater.* **2008**, *19*, 651–656. [[CrossRef](#)]
- 25) Vesel, A.; Zaplotnik, R.; Primc, G.; Mozetič, M. Synthesis of Vertically Oriented Graphene Sheets or Carbon Nanowalls—Review and Challenges. *Materials* **2019**, *12*, 2968. [[CrossRef](#)]
- 26) Yamamoto, S.; Kawana, A.; Masuda, C. Tribological behavior of diamond-like carbon produced by rf-PCVD based on energetic evaluation. *Surf. Coat. Technol.* **2013**, *236*, 457–464. [[CrossRef](#)]
- 27) Kaczorowski, W.; Batory, D.; Szymanski, W.; Niedzielski, P. Evaluation of the surface properties of PEEK substrate after two-step plasma modification: Etching and deposition of DLC coatings. *Surf. Coat. Technol.* **2015**, *265*, 92–98. [[CrossRef](#)]
- 28) Itoh, M.; Suda, Y.; Bratescu, M.; Sakai, Y.; Suzuki, K. Amorphous carbon nitride film preparation by plasma-assisted pulsed laser deposition method. *Appl. Phys.* **2004**, *79*, 1575–1578. [[CrossRef](#)]
- 29) Choi, J.; Ishii, K.; Kato, T.; Kawaguchi, M.; Lee, W. Structural and mechanical properties of DLC films prepared by bipolar PBI&D. *Daim. Relat. Mater.* **2011**, *20*, 845–848.