Krzysztof Jastrzębski
Division of Biomedical Engineering and Functional Materials,
Institute of Material Science and Engineering, Lodz University of Technology,
1/15 Stefanowskiego St., 90-924 Lodz, Poland, kj.doktorant@gmail.com

Aleksandra Jastrzębska
Division of Biophysics, Institute of Material Science and Engineering, Lodz University of Technology,
1/15 Stefanowskiego St., 90-924 Lodz, Poland

Dorota Bociąga
Division of Biomedical Engineering and Functional Materials,
Institute of Material Science and Engineering, Lodz University of Technology,
1/15 Stefanowskiego St., 90-924 Lodz, Poland

A REVIEW OF MECHANICAL PROPERTIES OF DIAMOND-LIKE CARBON COATINGS WITH VARIOUS DOPANTS AS CANDIDATES FOR BIOMEDICAL APPLICATIONS

Abstract

In the modern world, there is an increasing demand for implants, and technologies connected with their manufacturing. One of the possible paths of their development relates to the use of diamond-like carbon coatings (DLC) for the improvement of surface properties of the biomaterials used for implants. Further improvement of the mentioned properties can be induced by means of doping of the coating. Among the elements which are under current investigation of researchers, the following can be placed: Ag, Si, F, Cu, Ti, Ca and P. This paper reviews previously published experimental data concerning mechanical and physicochemical properties of DLC coatings doped with Ag, Si, Cu, Ti, Ca, F and P as candidates for biomedical applications. Although plenty of articles are published in the mentioned field, the differences of coatings' synthesis techniques, various sources of dopants and substrates, as well as conducted experiments make no consistent view about a possible solution for their future implementation in medicine. Some of the selected dopants (Cu, Ca, P), still require better characterisation of mechanical properties. There is a necessity to conduct studies of mechanical and physicochemical properties of DLC coatings doped with these elements. This will enable adjustment of the necessary technological parameters to biomedical requirements.

Keywords
Diamond-like carbon, doping, mechanical properties, thin films, biomaterials

Introduction
Modern world could not exist without a continuously developing health care system. Implants of various assignments, from bone stabilizers and prosthesis to peacemakers or artificial organs are in common use. Market requirements in that field are still growing both in case of number, as well as functionality of implants. Only in the case of orthopaedic surgeries, increasing demand for implants inserted each year is well visible. In USA, the annual increase of total hip and knee arthroplasty declared for 2010 was estimated to be on the level of 4.3% [1], while in England and Wales between 2008 and 2010 the number of such treatment increased from about 110 000 to 166 000 [2].

One of the crucial aspects of an interaction of a biomaterial with a tissue is through its surface. Both initial and long-term responses to a grafted material depend to high extent on its surface properties. Some of the main problems to overcome are unfavourable biological phenomena like those connected with the release of metal ions from the implant to the surrounding tissue leading to their deposition in tissues and organs (spleen, liver, blood, etc.), allergies or tissue irritation [3]. For this purpose, the use of biocompatible coatings seems to be a reasonable solution. The rapid development in this field concerns mostly the use of diamond like carbon (DLC) coatings. These coatings act as a diffusive barrier preventing tissue near implantation site from the penetration

of metal ions [4,5,6,7]. What is more, since carbon itself possesses a biocompatible character, it ensures the biocompatibility of the whole coated material. Recent studies moved even one step further. Through doping of DLC with various elements, new biologically significant features were obtained. Among dopants that have a high potential for improving the properties of coatings for implants there are: Ag, Si, Cu, Ti, Ca and P [8]. By the addition of Ag and Cu, the risk of post-operational complications involving yeasts or bacterial infections was reduced [9]. In the case of presence of Si and Ti in DLC coatings, the improved osteointegration of implant with host tissue was observed [10,11]. The aspect which is very important for cardiovascular grafts is prevention of clot formation. Such effect was observed for example using Ca, P or Si as a doping material [12,13].
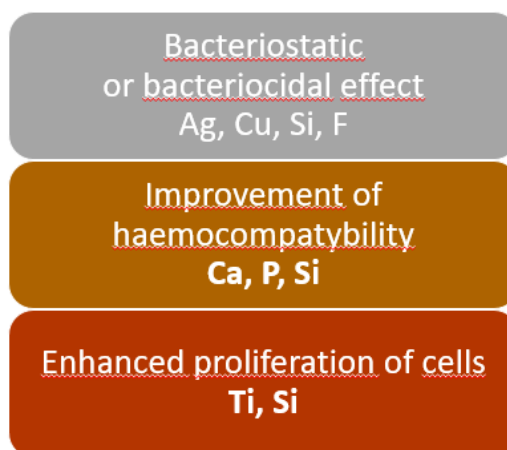
Fig. 1. Dopants of DLC coating for potential biomedical applications
Source: Author's

Although high impact was placed on the biological evaluation of the mentioned coatings [8,14], it should be remembered that even the best bio-features will not secure the success of the end product without appropriate mechanical and physicochemical properties. Living body is in fact a very hostile environment. Implants are in constant contact with severely corrosive biological solutions and body fluids. In orthopaedics, implants are commonly working under load-bearing conditions, where good adhesion of the coating and its wear resistance are crucial, otherwise wear debris become even more dangerous for the patient's health than the implant itself. Moreover, the proper mechanical properties are required not only during the initial stages of health treatment, but starting from the implantation process until the end of the patient's life. Considering the above, due to an increasing life expectancy of the population, the need of a fail-safe implant life span is also rapidly increasing.

There are already several published reviewing articles concerning undoped DLC coatings or focusing only on few of the doped derivatives [14-16]. In some publications, authors consider mostly only one aspect of DLC coatings, like their biological [8] or tribological properties [17]. The purpose of the present paper is to evaluate mechanical and physicochemical properties of DLC coatings doped with Ag, Si, Cu, Ti, Ca and P, i.e. the elements that can positively influence their potential for biomedical applications according to biological evaluation.

DLC Coatings
One of the commonly used generalizations is that DLC coating is build up as amorphous carbon with some sp3 bonds contained in its structure. In fact, this name stands for an entire range of various coatings with different ratios of sp2/sp3 fractions. What is more, differences in the hydrogen level in these structures are very high. In the literature, three abbreviations: ta-C, a-C and a-C:H, are typically used. The first one stands for tetrahedral amorphous carbon, a structure resembling diamond, and as a result – possessing the highest sp3 content. In the second case – the amount of amorphous carbon with a planar sp2 configuration is on the level close to sp3, and lays in the range of 20 to 60%. The last option covers the coatings with a high amount of hydrogen, which is usually related to the presence of higher amount of sp2 bonds. The type of obtained DLC is highly dependent on the manufacturing technology [2,15], which at the same time provides different coating properties of such as different internal stresses or coefficients of friction [13,18].

The common drawbacks of DLC coatings are: high internal stress [16,18,19] and degradation of mechanical properties due to heat treatment [20]. It should also be remembered that because of high internal stresses, an additional problem concerning coating's delamination may appear. There exists a relation between the level of internal compressive stress and the sp2/sp3 ratio. It shows that the presence of high amount of sp3 bonds in the material (above 80%) leads to higher stress values that can even reach 10 GPa [22].

Influence of synthesis method and process parameters on DLC properties
In the beginning of 70s, the first studies leading to synthesis of DLC coatings were conducted with the use of ion beam deposition by Aisenberg and Chabot [23]. From that time, various techniques including magnetron sputtering, laser ablation, chemical vapour deposition etc. were investigated. The mechanical and physicochemical properties of synthetized DLC coatings depend both on the process parameters and the production technique itself [15,16]. Trava-Airoldia et al. [26], showed that a significant difference between hardness, tribological properties, total internal stress and adherence of DLC synthetized by r.f. PACVD, IBAD, and Enhanced Pulsed-Direct Current PECVD (EP-DC PECVD) appears, even if all manufactured coatings are of the same thickness. The mentioned coating properties were described as a function of self-bias voltage, ion beam current, and pulsed-bias, respectively for each method. Although in all cases Raman spectroscopy revealed an increase of ID/IG ratio with the increase of self-bias and ion current, the degree of graphitisation of the coating varied among the techniques. In the case of evaluation of total compressive stress of DLC, the highest value of that parameter was usually obtained for intermediate process parameters (voltage bias or current). The lowest compressive stress was obtained for the highest negative voltage bias in case of PACVD method and highest current of IBAD processes, but lowest negative voltage bias in EP-DC PACVD method. The exact values of stress differed from about 0.5 up to 3 GPa [26]. The influence of the substrate material on the evaluated compressive stress was also visible. The difference between stress of coatings synthetized on silicon wafer and Ti6Al4V substrates with an amorphous silicon interlayer was higher than 0.5 GPa. It must also be remembered that the method of coating synthesis also affects the technical aspects of the process, for example different deposition rates, which may differ in suitability for laboratory and industrial scales of coating manufacturing.

In the case of synthesis of DLC by CVD methods, a crucial aspect was also a selection of the carboniferous gas which also could influence the rate of coating deposition [27]. Gases introduced to the chamber could additionally affect DLC deposition by magnetron sputtering. Data presented by Libardi et al. [28] showed that in general, the highest hardness of coatings had been found at approximately 10% of hydrocarbons content. Nevertheless, lower hardness of films was obtained when acetylene was used rather than methane. What is more, gas composition inside the chamber affected surface roughness, which was the lowest for methane/argon mixture. In the literature, DLC roughness was also related with temperature of the surface [29] or impingement energy of ions [30].

Even in the case of processes conducted with the same technique and with the use of the same substrate, DLC coatings could reveal different properties depending on detailed parameters of the synthesis, for instance, in studies concerning synthesis of DLC by radio frequency (RF) magnetron sputtering conducted by Chowdhury et al. [31,32]. In the study, the influence of substrate temperature and of target self-bias voltage on the mechanical properties of the coating were examined. It was observed that not only hardness and Young's Modulus of the DLC layer, but also internal stress and ID/IG ratio were affected.

Doping of DLC
In order to overcome the existing problems with some mechanical, physicochemical or biological properties of DLC coatings or for their improvement, the use of various doping elements and materials is common. In the literature, not less than 26 various dopants of amorphous carbon films can be found [25,31,32]. Studies involving multiple dopants have already been conducted to adjust the DLC parameters to an even higher extent.

In current scientific publications, the following nomenclature is typically used: the dopant atom is written as the first one and is separated from DLC abbreviation by a dash. In case when interlayers appear, they are

separated by a slash. However, in many cases the information about the interlayer is given only in a descriptive way.

The introduction of the dopant element is usually performed with the sputtering of the solid target, or vaporization of solid or liquid material. The selection of dopant's source depends to a high extent on the selected method of DLC deposition. In some cases, additional restrictions concerning corrosive or flammable character of some compounds had to be taken into account. The most common approach to DLC doping, both in laboratories and industry, is by the use of sputtering methods or Plasma-enhanced chemical vapor deposition (PECVD). In the first case, techniques were selected mostly due to their simplicity and possibility of using wide range of targets, both conducting and non-conducting. DLC can be synthetized by DC or RF sputtering of graphite [35,36], pyrolitic carbon [37] or even diamond powder [38] in an argon plasma. In some studies, the reactive atmosphere was used. This means that hydrogen or hydrocarbons in a gaseous form were additionally introduced into the chamber during the deposition. The major drawbacks of sputtering methods are relatively low rate of coating deposition (on the level of few nanometers per minute), contamination of targets in reactive processes or concomitant sputtering of several targets of different materials [27,39]. In general, PECVD method requires a formation of plasma between two electrodes. Usually one acts as a table for mounting samples, while the walls of the chamber act as the second one. The precursors of both carbon and dopant elements are introduced in gaseous forms. The major advantage of such technique is the possibility of uniform coating deposition for large areas or complicated shapes. On the other hand, however, selection of precursors could be problematic for all the dopants that should be in a gaseous state or easily evaporative compounds, containing in their structure only element of interest and carbon (so as not to contaminate the coating with an unwanted element). In many studies, also hybrid methods were introduced, which enabled to partially overcome the limitations of each separate technique.

Among the fields of DLC improvements, which are under constant investigation of researchers all around the world, predominantly there are: tribological behavior, adhesion, surface energy, biological response, optical and electrical properties. Low coefficients of friction were obtained mostly by incorporation of F [40] and Si in DLC coatings [41], but also metals like tungsten, especially in presence of high temperatures [42, 43]. One of the common operations to improve DLC adhesion is with the use of interlayers. In this case not only single and multilayers, but also gradient ones were introduced [44,45]. Among the elements responsible for altering the hydrophobic/hydrophilic properties of DLC numerous dopants, both metallic and non-metallic like: Si, F, O or N were used [46]. As far as biological response is concerned, the most important aspects are biocompatibility, osteointegration, haemocompatibility or antimicrobial activity. The electrical resistance of doped DLC did not change linearly with the addition of dopant. This is because DLC can be treated as an amorphous semiconductor. The concentration of additive atoms must be large enough to form continuous channels for electron transport. Introduction of n-type impurity into DLC films (electrons close to conductive band) could improve the field emission performance. Studies concerning this field used for example N, P or Ti as doping elements to obtain the desired results [47-49]. Optical properties were related with high transparency of undoped DLC under infrared and ultraviolet radiation. With doping, change of refractive index of the coating could be achieved in a precise way [50]. This means that such films could be used for manufacturing of protective optical coatings against infrared radiation.

In the further discussion, only selected elements with possible beneficial effect on DLC coatings used in biomedical applications will be described more extensively. The main focus is placed on the tribological properties as well as hardness and surface morphology of the coatings.
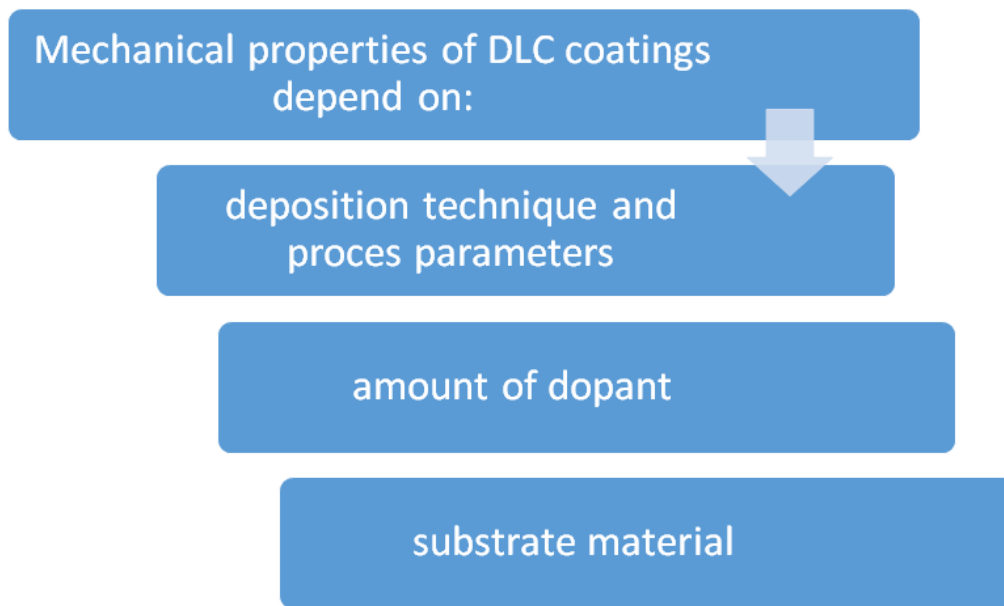
Fig. 2. Major factors affecting mechanical properties of DLC coatings
Source: Author's

Silver

Ag is a material, known for ages to possess very important biological feature - helping to fight against microbial infections. Because of this, its use as a dopant element for DLC coatings is obvious when biomedical applications are concerned. A wide number of PVD and CVD methods were used to incorporate this dopant into the DLC film, and these are: various types of sputtering techniques, plasma source ion implantation, radio frequency plasma enhanced vapour deposition, etc. [51-54]. Magnetron sputtering methods involved the use of pure Ag target [55,56] or metal pellets/bars [57] placed on the target serving as a carbon source. In some studies, Ag nanoparticles were also used. As far as the substrate material is concerned, many solutions were introduced, from glass or silicon wafers [55,56] to metallic materials [52,53]. Also, the use of interlayers like pure Si or Ti/TiN/TiCN has been evaluated [51]. Very high variations occurred also in the amount of doped Ag which typically can reach about 30%. However, Takeno et al. [54] obtained DLC composites with Ag content reaching as high as 84%.

In the case of coating synthesis by means of magnetron sputtering in the presence of argon and gaseous carbon source (methane [58], or acethylene [54]), the unfavourable adsorption of hydrocarbon onto the target surface and as a result, decrease of sputtering yields, was observed. On the other hand, by means of such phenomena, it was possible to alter the composition of the formed coating only by controlling the ratio of target poisoning/volume of the source gases. For pure magnetron sputtering, Ag concentration could be increased by application of high power to the target [56].

As far as mechanical properties are concerned, in general the presence of Ag decreased the hardness of DLC coatings. This effect was concomitant with the reduction of internal stress of the layer [57]. Wu et al. [57] and Manninen et al. [58] noticed, that in case of low amount of dopant (below 3%), the depletion in hardness can be negligible in comparison to undoped DLC. For over 10% of Ag, the drop in hardness became significant and could even decrease to 60% of the original value (similar depletion was observed for the value of Young's modulus). Reduced hardness could be explained by the fact that Ag did not build in amorphous matrix, but formed independent units of soft crystalline structure. What is more, it increased the amount of sp2 bonds [51], which do not provide the high hardness values.

Ag in DLC films is claimed to appear commonly in form of aggregates or clusters. The images of an Ag-DLC surface showed no changes in surface structure for very low amounts of Ag, however a granular character or even separated islands of dopant material were observed when Ag content exceeded 3.5% [55]. Investigation of Ag clusters with X-ray diffractometry (XRD) by Meškinis et al. [51], revealed that Ag-DLC with low dopant content (1.3%) predominantly contained crystalline Ag oxide rather than the noble metal itself. Only in films

with high concentration of Ag, crystallites of various orientations were discovered. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) examinations showed that the roughness and size of agglomerates increase with higher amounts of this dopant [54, 56]. One of the observed phenomena was also surface segregation of Ag with time [57]. It could lead to transformation of Ag-clusters into Ag-aggregates, and as a result influence the tribological properties of the coating.

In many cases, the dopant of soft material like Ag acted as a solid lubricant and lowered coefficient of friction [59,60]. Although Ag was usually not mentioned as a dopant leading to improved tribological properties, Yu et al. [61] claimed that Ag addition by multi-ion beam assisted deposition led to a reduction of the coefficient of friction (CoF) of the coating. These data are contradictory to studies of Manninen et al. [57], who synthetized Ag-DLC by unbalanced magnetron sputtering and obtained worse tribological properties than for undoped DLC. These two studies are examples of how various properties of undoped DLC used as a reference can influence the interpretation of the conclusive results. DLC coatings prepared by magnetron sputtering exhibited CoF on the level of 0.06-0.1 [57], while those synthetized by multi-ion beam assisted deposition had a CoF equal to 0.2 [61]. Nevertheless, in both studies (conducted under dry conditions with ball-on-disc technique), values of coefficient of friction were in the similar range, from about 0.1 to 0.2. Tendency of CoF change with increase of dopant concentration is also interesting. Manninen et al. [57] obtained an almost linear increase of coefficient of friction with an increased amount of Ag, but Yu et al. [61] showed that the lowest value could be related with an intermediate concentration between 6 and 12%. Very low CoF of Ag-DLC was obtained by Wu et al. [58]. The experiments were conducted in vacuum (10^{-3} Pa) and resulted in CoF reaching values of only 0.005. The wear resistance was depleted by the presence of Ag as a dopant. It is interesting taht in the mentioned studies, with higher amount of Ag and under lower contact pressure (690 MPa) wear rate of the coating increased only slightly , but under increased contact pressure (1180 MPa) it highly increased. Tribological tests conducted with Ag-DLC showed a formation of Ag layer on the counterpart [57]. This phenomenon was claimed to affect the tribological behaviour in different ways. On one hand, interactions of a transfer layer with aggregates of Ag in the wear track might result in increased coefficient of friction. On the other hand, graphitization of carbon could take place, leading to better lubrication properties of the coating and thus reduced coefficient of friction.

No clear dependence between Ag concentration and coating adhesion was reported. Some data state that the improved value of critical load could be obtained for all Ag concentrations within the range of about 1% to 13% [57]. Other studies showed a significant decrease of this parameter for higher amounts of Ag [52].

As the wettability is concerned, the doping with Ag led to increase of contact angle in the case of polar solvents, showing a hydrophobic character of the coating. At the same time, the drop of surface energy was observed [54,56]. However, it seems that such effect was not only the result of the dopant element itself, but also of the increased surface roughness.

Copper
Although Cu as a dopant possesses similar features as Ag, its use as additive for DLC is much less popular, even in the field of biomedical applications. Therefore, also the mechanical and physicochemical characteristics of Cu-DLC coatings are described less precisely. Introduction of Cu was performed by means of reactive magnetron sputtering, PECVD, cathodic arc deposition or by hybrid methods [62-66]. Hussain et al. [67] reported even introduction of both Cu and Ag into DLC by electrochemical technique involving use of various amounts of salts containing these elements. In the case of processes involving sputtering, the rate of deposition of Cu-DLC films was increased by increasing the plasma power, which is a typical effect for such techniques. Silicon wafers were commonly used as a substrate material, nevertheless studies concerning steel were also conducted, though in lower number.

Similarity with Ag-DLC was observed in the morphology of the coatings with Cu dopant. According to Tsai et al. [63], Cu-DLC exhibited spherical clusters of nanocrystalline particles which increased surface roughness. On the contrary, Chaus et al. [65] claimed that these coatings had a smooth surface with a roughness of 2–4 nm, having only some nanoinclusions of oxidized Cu. However, XRD analysis of Cu-DLC did not reveal the presence of high amounts of CuO [62].

The deterioration of mechanical properties of Cu-DLC was observed in comparison to undoped DLC. Commonly, hardness and Young's Modulus of Cu-doped amorphous carbon coatings were depleted with increased concentration of the doping element. Only the single study of Tsai et al. [63] claimed the increase of these parameters as a result of Hall-Petch hardening. What is more, introduction of Cu promoted sp2 bonding [64]. By means of reciprocating sliding tests, a four-times increase of Cu-DLC coefficient of friction (up to 0.23) was observed in comparison to undoped DLC (0.06-0.07) [65]. In these studies, the sliding wear also increased.

Among the improved parameters of Cu doped DLC, also a temperature dependent electrical conductivity, which can even reach a three orders higher conductivity than undoped DLC [62]. Reduced value of residual stress of the coating was observed in Cu-DLC by Pardo et al. [65] and Chan et al. [66]. Similarly as in the case of Ag-DLC, the water contact angle of the Cu containing coatings has increased compared to undoped DLC [63].

Silicon
Si-DLC is a material very important from the tribological point of view. Due to the very low friction coefficients exhibited by this material in humid atmospheres as well as at high temperatures, it was vastly investigated all over the world [41]. In CVD methods, Si-DLC was synthetized with the use of organic precursors like hexamethyldisiloxane [68] (in this case, SiO-DLC was formed), tetramethylsilane [69] and toluene [70]. It could also be obtained by sputtering of a Si target [71]. The wide range of studies were also conducted with numerous other substrate materials.

Although plenty of studies in the field of Si-DLC were conducted, many questions concerning the most basic mechanical properties still exist. Hardness and Young's Modulus of Si-DLC seem to be highly dependent on the concentration of Si in the coating. The complex studies conducted by Wang et al. [72] on films with Si content up to 14.8% showed almost no deterioration of the mentioned parameters for low Si contents (up to about 8.4%), but showed improvement for higher Si concentrations. The film containing maximum amount of dopant had a hardness above 22 GPa. In studies of Bendavid et al. [69] and Zhao et al. [73], a deterioration of hardness with an increase of Si content in the films was also observed – in both cases, decrease of coating hardness and Young modulus was observed for Si concentration not exceeding 5%. Although in the mentioned studies, the hardness of undoped DLC were about 14 and 25 GPa, respectively, , hardness values stabilised on the level of 11-12 GPa with the increase of the amount of dopant. In all three mentioned cases, PACVD method was used to synthetize the coatings. In another study, Fujimoto et al. [74] related hardness with voltage of pulse-plasma chemical vapour. In this case, -5kV of pulse voltage led to increase of coating hardness (Si content was above 5% but lower than 25%), while -2kV pulse voltage decreased the hardness (Si content was about 20%). Also in other published works, hardness was not correlated directly with the dopant concentration, but other process parameters, for example temperature of gases in the chamber [75].

The concentration of Si highly influences the already mentioned tribological parameters of Si-DLC coatings. Wang et al. [72] presented results in which low dopant content resulted in an unstable value of coefficient of friction, that could be even higher than for undoped DLC. For high dopant contents (above 11%), a low coefficient of friction (below 0.1) was obtained. Such results correlate with the data presented by Hofmann et al. [76]. In this study, CoF of Si-DLC was on the level of 0.15 for Si concentrations below 10%, while it decreased to 0.1 when dopant content was in the range of 10-25%. Also Ikeyama et al. [70] obtained the highest coefficient of friction of 0.25 for the lowest concentration of the dopant (below 1%). With an increase of Si content, CoF decreased, however this study was conducted only for Si concentrations below 10% (minimum CoF was 0.12). Low friction was claimed to be a result of the hydrated silica debris present in the track [77]. According to Kim et al. [79], only for high Si concentrations, enough SiO was present on the surface to significantly reduce the coefficient of friction. On the other hand, Gilmore et al. [78], studying the influence of moisture content on tribological properties, showed that even small amounts of Si in the coating, like 1.6 to 5.7%, could lead to a reduced coefficient of friction on the level of 0.07-0.08. Such data were obtained only for humidities between 5% and 65%, while for 85%, the CoF values were slightly higher, in the range of 0.08-1.00. In fact, for low humidity (5%), Si content of 22.1 and 35.5% led to higher CoF, between 0.55 and 0.60. Nevertheless, in 65% and 85% humidity, its value decreased to the level of 0.60.

The wear rate (described as wear surface volume divided by the load and total distance travelled by the counterface steel ball), decreased with the increase of Si concentration in the DLC coating. However, only for high amounts of Si, wear volume was lower than for undoped DLC [72]. On the other hand, in another study

[70], depth of the sliding trace decreased with the increase of Si even for low dopant concentrations. Results presented by Hofmann et al. [76] and Kim et al. (1999) [77], showed a continuous increase of the wear rate with higher amounts of Si. The influence of corrosive environment resembling body fluids on the wear resistance and friction coefficient was also examined by Kim et al. (2008) [79], however, only for low Si contents. The presence of 0.89% of NaCl during tribological tests increased the coefficient of friction in all cases. In wear-corrosive examination, devastation of the material occurred through blistering, which led to a much higher material breakdown than in a standard wear test. Corrosion rate was evaluated in corrosive and wear-corrosive environments. It was shown that abrasion related to the presence of NaCl solution led to a formation of a galvanic cell between the wear tack and the unworn surface, which resulted in massive increase of the corrosion rate.

As far as the morphology and the topography of Si-DLC are concerned, the resulting surfaces possessed a granular structure, and the roughness increased with the addition of the dopant [72]. As stated by Jones et al. [80], Si-DLC coating could to some extent even cover the inside of pits on the substrate material. It also significantly minimized the penetration of NaOH regardless of the Si content. Connected with this fact is also a good resistivity of the coating in 0.05M NaCl solution confirmed by the potentiodynamic polarization experiments [81]. The electrochemical test also showed that the coatings with higher Si content absorbed less water and ions from the corrosive environment than the coatings with lower Si content [73,79].

DLC with incorporated Si expressed lower compressive stress than an undoped DLC. In contrast to Ag-DLC and Cu-DLC, the addition of Si stabilised the sp3 fraction [81].

Fluorine
Similar to other already mentioned dopants, F was also incorporated into DLC coatings by means of various methods like cathodic vacuum arc evaporation [82], reactive magnetron sputtering [83], PECVD [84] etc. It was introduced to the process chamber in form of gaseous precursors.

Freire et al. [85] conducted studies on F-DLC films synthetized by PECVD, in which dopant concentration did not exceed 19%. Deposited coatings expressed hardness in the range of 5-6 GPa. Similar results were obtained by Bendavid et al. [86], but for a maximum 40% concentration of the dopant. In this study, for 20% of F, coating hardness was on the level of 8 GPa. In both cases, hardness of undoped DLC was similar (15-16 GPa). To increase the hardness of F doped DLC, co-doping with boron can be conducted. BF-DLC films were synthetized with plasma immersion ion method by He et al. [78]. These coatings were prepared on four substrates: silicon, glass, polymethyl methacrylate and polycarbonate. Films on the first two materials a had hardness of over 17 GPa for F content of up to 10%. For higher F concentrations, it was at least 15 GPa (in both cases concentration of boron was fixed to about 4%). Unfortunately, no data concerning the tribological properties of BF-DLC were provided.

Research conducted by Donnet et al. [88] showed a strict correlation between the amount of F and the mechanical properties of F-DLC coatings, especially their wear resistance. When the ratio of F/(F + C) was lower than 0.2, the wear resistance was similar to undoped DLC and could be tailored by adjusting the deposition conditions (high deposition bias, low gas pressure etc.) [85].

In work of Sung et al. [40], the name "dialon" appeared for fluorinated DLC. It stands for diamond-teflon material fabricated by RF PECVD method, with a friction coefficient of less than 0.001. On the other hand, Wang et al. [89] examined DLC terminated with F. Quantitative calculations of such coating models had a CoF between 0.08 and 0.09. Experiments performed on the material sample showed that F content in the range of 1-20% led to a gradual reduction of coefficient of friction to the level of 0.12 [85].

As far as the roughness of the F doped DLC coatings is concerned, addition of this dopant led to an increase of this parameter [83]. In the literature, such tendency was correlated with etching of the surface during PECVD process [90,91].

F-DLC is a hydrophobic coating, where water contact angle can reach over 90° [83]. Saitoa et al. [84] examined values of contact angle with human blood and obtained an almost 4-times increase of this parameter in comparison to the substrate material, which was silicon. With an increasing amount of the dopant, a decrease

of the total surface energy and its dispersive component was observed. Value of polar component was growing due to the presence of more unsaturated bonds on the surface (coating graphitisation). Bonds from the F-DLC surface (lower amount of –C–CF, and higher amount of –CF and –CF$_2$) were identified as a reason for the drop of dispersive component of surface energy [74, 81]. Raman spectroscopy in studies of Marciano et al. [92] and Bendavid [86] et al. showed an increase of ID/IG ratio of coatings with higher amounts of F. The incorporation of this dopant also reduced the compressive stress of DLC layers.

Addition of F also had a positive influence on DLC electrochemical corrosion resistance, which was evaluated by potentiodynamic polarization test by Marciano et al. [92]. Less than 2% of the dopant reduced corrosion current density by more than one order of magnitude in comparison to the undoped DLC films.

Titanium

Ti is the most commonly used dopant of the seven elements selected for this review. This is why in the literature, various techniques were used to incorporate it into the DLC matrix [92-97]. Moreover, precise evaluation of synthesis parameters and of mechanical properties of these coatings have been done in many cases. The process of coating synthesis could also involve fabrication of single or multiple interlayers concerning pure metal, its carbide or other compounds [98]. Ti-DLC was synthetized on various substrates, both metallic and non-metallic ones. To obtain improved properties also multi-dopant systems were used, for example by using Ti and Cr [99].

X-ray photoelectron spectroscopy (XPS) proved that Ti was incorporated into the amorphous carbon structure in form of titanium carbide (TiC) nanoparticles for high dopant content. The exact percentage of Ti that could dissolve in DLC varies in the literature from 0.9 and 2.5 up to 16% [100,101]. Dai et al. [102] claimed that Ti reduced compressive stress when it was present in low amounts, but increased it when its content in the coating exceeded 8%. Such phenomenon was correlated to the already mentioned solubility of Ti in DLC matrix. When this element was uniformly distributed in a matrix, it acted as a pivotal site for occurring distortions of atomic bonds. High Ti content led to a formation of Ti-C bonds which were longer than conventional C-C ones, so that the compressive stress of the coating was increased.

There are no consistent data concerning the influence of low amounts of Ti on sp2 and sp3 fraction. By means of Raman spectroscopy, Qiang et al. [103] evaluated that doping of DLC with Ti decreased the sp3/sp2 ratio for low concentrations of the dopant, but Dai et al. [102] provided opposite results: for higher addition of Ti, graphitization of the coating occurred, and this phenomenon was related with the increase of sp2 hybridization of carbon by Qiang et al. [104].

Looking at the change of sp2/sp3 ratio due to doping with Ti, it could be assumed that generally hardness would drop because of the graphitization process [94,97]. Nevertheless, part of the literature, for example data presented by Ma et al. [93], showed just the opposite. The reason of such state was claimed to be the increasing presence of hard TiC nanoparticles, which not only alleviated the higher amount of sp2 fraction, but also further increased the coating hardness. As far as the process parameters are concerned, hardness of DLC coating increased after doping with Ti and with increasing substrate bias [105]. When at the same time target-substrate distance was considered, for high voltage bias hardness was increasing with a higher separation of the substrate and the target. For low substrate voltage bias, hardness decreased for processes conducted with higher distances. In general, experiments involving high power plasma magnetron sputtering revealed that substrate-target distance rather than substrate bias has a predominant effect on Ti content and hardness. Taking the above into consideration, hardness of Ti-DLC was the result of not only Ti concentration but also of the parameters of the synthesis process.

The morphology of Ti-DLC surface depends on TiC formation process. The formation of micro and sub-micro sized nanoparticles led to a roughening of the surface [94]. Moreover, in the case of low Ti content, the smoothness of undoped DLC was almost maintained [103].

By the experiments involving ball on disc test, higher adhesion of the coating to the metal substrate was claimed [102]. This was also confirmed by means of a scratch test (even a 3.5-time improvement of the adhesion strength) [94]. Moreover, Ti-DLC was characterised by a reduced coefficient of friction (to 0.2-0.1 [97] or even 0.04 [103]). As Gilmore et al. [78] showed in their study, the difference between CoF obtained for

humidity of various values can be higher than 0.05. The lowest coefficient of friction (below 0.05) was obtained for the lowest humidity (5%). When wear resistance of the coating was concerned, the best solution was to limit the amount of doping [94]. The presence of TiC nano and microparticles led to abrasion of the material. Ball-on-disc testing with steel balls as counterparts showed high wear rates and unusual W-shape wear tracks [102]. Such shape was present due to the occurrence of high amount of wear debris originating from the counterpart.

The addition of Ti also influenced the hydrophobicity of the coating surface. Increase of water contact angle (to 130°) was observed in contrast to undoped DLC (70°) [93]. Ti was also responsible for the decrease of the resistivity of the doped coating [106].

Calcium

There are not many studies concerning the use of Ca as a dopant material for DLC coatings. In the literature, mostly incorporation of calcium oxide rather than undoped Ca was considered. Moreover, the published studies were focused on biological evaluation and not mechanical properties of the obtained coatings. Only two different methods were used for the synthesis of these layers.

The first attempts to develop DLC with Ca or its derivatives were conducted using a direct current discharge by Dorner-Reisel et al. [107,108]. Gases used during the coating fabrication were methane and CaO-H$_2$O vapours. In the case of this method, decomposition of both hydrocarbon and Ca precursors took place in the synthesis chamber. As a result, Ca was introduced to the Ca-O-DLC in form of carbonate, which was confirmed by the data obtained with XPS and IR-spectroscopy. The rate of deposition reached about 16 nm per minute which was lower than in the case of undoped DLC (about 19 nm per minute). Studies involving this method provide a good description of both basic mechanical and biological properties of these coatings. What is more, the synthesis was conducted on a metal substrate – Ti6Al4V, which shows a possibility of future implementation of such technique for implants. Authors claimed that the presence of Ca in the coating led to a drop of hardness, Young's Modulus and relative elastic recovery of the coating. On the other hand, with the increase of CaO-H$_2$O partial pressure, the difference between mechanical properties of doped and undoped DLC decreased. With the addition of Ca-O to the DLC matrix, the adhesion of the coating was improved. The major drawback of the presented studies is that Ca content was estimated only by considering the partial pressure of CaO-H$_2$O and no quantitative estimation was made.

The second technique of incorporation of Ca to DLC coating was based on plasma immersion ion implantation and deposition (PIII and D), with the use of a pure Ca powder [109]. The mixed gas plasma was obtained by evaporation of Ca with the addition of acetylene and argon. Unfortunately, the physicochemical examination of coatings synthetized this way was narrowed only to evaluations of contact angle, interfacial energy between samples and water, and elemental depth profiles obtained with XPS. XPS showed a stable Ca concentration (on the level of about 10%) within the depth of 60 nm, while a rather sharp interface between carbon (from the coating) and silicon (from the substrate material) was observed at around 25 nm.

Phosphorus

Similarly as in the case of Ca, not many studies were devoted to the investigation of phosphorous doped DLC. These investigations covered synthesis of films with the use of phosphane (-PH$_3$) gas [110] or evaporated red P powder [109], while the common techniques are PIII and D and filtered cathodic arc method. One of the interesting experiments involved formation of a target for the pulsed laser deposition in form of pellets made of burned camphor mixed with various amount of red P [47]. Since doping of DLC with P was mostly targeted on obtaining better electronic properties of the coating, the majority of published data did not thoroughly describe the mechanical properties, usually only the increase of roughness in comparison to the undoped DLC was denoted [112]. Some additional studies involving multi-dopant DLC coatings with both Ca and P were published, yet they focused on biocompatibility and hemocompatibility [109].

The studies were mostly concerned with the low amount of doped P – on the level of 0.2-3%, but in some cases the atomic concentration on the surface reached almost 20%. The addition of about 1 % of P was claimed not to alter the tetrahedral network of bonds present in the DLC coating, however only 3% of this dopant increased the amount of sp2 bonds [113]. P-DLC exhibited several orders of magnitude lower resistivity than undoped

DLC. Data concerning hardness showed better properties of P doped DLC, but not in a linear dependence with the dopant concentration. Maximum value of hardness (9.34 GPa) at 50 gm load was obtained for 1% P-DLC. All studies showed a very good wettability of P-DLC coatings with polar solvents (in some studies, the contact angle value was only 17°) [112, 113].

One of the characteristic features of P doped DLC is its microstructure resembling numerous dots evenly distributed on the surface, as presented by Kwok et al. [113]. Their parameters could be averaged to about 8-18 µm of diameter and 20-50 nm of height. The conducted chemical composition evaluation by means of energy-dispersive X-ray spectroscopy (EDX) allowed to determine that only the spots contained P.

Little data concerning the rate of deposition of P-DLC has been reported. The use of phosphine could alter it from about 15 up to about 35 nm per minute. What is interesting, the highest improvement of the growth rate was observed for the low flow of PH_3 (maximum improvement of about 25% occurred for just 1.25% of P precursor concentration) [110].

Discussion

Although there are many studies concerning doping of DLC coatings with Ag, Si, F, Cu, Ti, Ca and P, it was complicated to compare the obtained results. The reason for this is related with a variety of techniques used for fabrication of coatings by research groups from all around the world, which result in different properties of even undoped DLC. What is more, numerous studies were conducted on silicon wafers and not on metallic substrates. Data obtained in this way may be promising, but for the sake of biomedical applications, the obvious requirement is the use of materials commonly available on the market of implants and/or medical equipment (titanium alloys, 316L steel, etc.). Only such studies can be fully informative and enable estimation of implementation possibility of the developed technology to the medical use.

Table 1. Comparison of the influence of the dopant concentration on the hardness of doped DLC coatings

Doping element	Dopant effect on hardness in comparison to undoped DLC	Hardness range of doped DLC
Ag	reduction of hardness	from ~7.5 GPa (~3.5at.%) to ~4.5 GPa (~11.0 at.%) [58] from ~13.0 GPa (~2at.%) to ~9.5 GPa (~13.0 at.%) [57] from ~13.0 GPa (~4.5at.%) to ~11.0 GPa (~15.0 at.%) [52]
Cu	reduction of hardness	from ~24.0 GPa (~5.0 at .%) to ~13.0 GPa (~30.0 at.%) [65] from ~16.0 GPa (~11.0 at.%) to ~15.0 GPa (~23,0 at.%) [66]
	no data	from ~2.75 GPa (no exact data) to ~3.25 GPa(no exact data) [63]
Si	reduction of hardness	from ~12.5 GPa (~4 at.%) to ~12 GPa (~13.0 at.%) [69] from ~20.0 GPa (~2.5 at.%) to ~13.7 GPa (~22,0 at.%) [73]
	increase of hardness	from ~12.0 GPa (~7.0 at.%) to ~22.0 GPa (~23,0 at.%) [72] from ~16.0 GPa (~7.5 at.%) to ~18.7 GPa (~22,5 at.%) [74] from ~24.0 GPa (~5.0 at.%) to ~27.0 GPa (~25,0 at.%) [76]
F	reduction of hardness	from ~16.0 GPa (~6.5 at.%) to ~6.0 GPa (~39.0 at.%) [86] from ~18.5 GPa (~12.5 at.%) to ~16.0 GPa (~37.5 at.%) [91]
	increase of hardness	from ~5.5 GPa (~3.0 at.%) to ~7.0 GPa (~19.0 at.%) [85]
Ti	reduction of hardness	from ~20.0 GPa (~1.0 at.%) to ~12.5 GPa (~4.0 at.%) [96] from ~27.5 GPa (~2.0 at.%) to ~17.5 GPa (~20.0 at.%) [97] from ~13.0 GPa (~0.5 at.%) to ~10.0 GPa ~8.0 at.%) [94]
	increase of hardness	from ~15.0 GPa (~5.0 at.%) to ~22.0 GPa (~24.0 at.%) [94] from ~10.0 GPa (~5.0 at.%) to ~20.0 GPa (~40.0 at.%) [100] from ~20.0 GPa (~4.0 at.%) to ~27.5 GPa (~24.0 at.%) [102] from ~30.0 GPa (~1.0 at.%) to ~32.0 GPa (~6.0 at.%) [106]
Ca	reduction of hardness	from ~18.0 GPa (no exact data) to ~9.5 GPa (no exact data) [107]
P	no effect	about 9 GPa (from 0.5at.% to 2.0at.%) [112]

Source: Author's

The addition of dopants described in the following article affected (i) the mechanical properties of DLC coatings: hardness (see table 1.), adhesion etc.; (ii) tribology (see table 2.) and (iii) also morphology or surface

energy of the deposited coatings. Comparison of the influence of dopant concentration on the hardness of doped DLC coatings presented in table 1. shows that no clear trends how Si, Ti and F affect even a single, most basic property of the fabricated coating such as hardness can be recognised, because both reduction and improvement of this parameter was reported in comparison to undoped films. The described values of hardness of doped DLC coatings were in the range from about 2.5 GPa to over 30 GPa. Only in the case of Si-DLC and Ti-DLC the hardness of films was higher than 10 GPa for all the described concentrations of the dopant. From this point of view, doping of DLC with these elements has the highest potential in biomedical applications requiring superior mechanical endurance (e.g. for orthopedic implants). With these elements also a reduction of coefficient of friction was observed, which may be advantageous in friction joints such as hip or knee prosthesis.

In predominant number of the presented studies, the examination of mechanical and physicochemical properties of doped DLC coatings was performed for samples with concentration of dopant element higher than 4 at.%. Since biological properties can be highly affected even with very low concentrations of the doping element [114], mechanical properties of such films should also be examined.

Properties of P-DLC and Ca-DLC are the least described. Tribology of these coatings was so far under minor investigation of researchers (see TABLE 2). What is more, the descriptions of other mechanical and physicochemical properties of P-DLC and Ca-DLC are also rather limited - authors focused primarily on the evaluation of their biological aspects. Lack of vast examination considering major functional properties of P and Ca doped DLC films prevented from objective evaluation of their biomedical potential.

Table 2. Comparison of tribological properties of doped DLC coatings with undoped films

Doping element	Increased CoF	Decreased CoF
Ag	YES*	YES*
Cu	YES	
Si		For high concentration
F	YES*	YES*
Ti	For high concentration	For low concentration
Ca	No data	No data
P	No data	No data

*Source: Author's. * Depends on the properties of undoped DLC coating*

Conclusions

Undoubtedly there are numerous studies considering the properties of doped DLC films which are reported in the available literature, and the stage has been reached at which tailoring of the properties of fabricated films should be considered for biomedical applications. In the present study, DLC coatings doped with Ag, Si, F, Cu, Ti, Ca and P are investigated in terms of mechanical and physicochemical properties regardless of their deposition technique or substrate material, which provides a wide range of functional properties that are achievable. Nevertheless, detailed studies considering the fabrication of coatings with various dopants and different deposition techniques are necessary to enable a direct comparison of the influence of each element. More experiments should be performed with the use of substrate materials common for biomedical applications: metallic polymeric and ceramic. This way, the studies could be easier correlated with the ways of their implementation in the industry.

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