We are IntechOpen, the world’s leading publisher of Open Access books
Built by scientists, for scientists

6,600
Open access books available

177,000
International authors and editors

195M
Downloads

154
Countries delivered to

TOP 1%
Our authors are among the most cited scientists

12.2%
Contributors from top 500 universities

WEB OF SCIENCE™
Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com
Abstract

One way to obtain new materials with different properties is to modify existing ones to improve their inadequate properties. Due to the fact that many useful properties of materials, including resistance to wear and corrosion, coefficient of friction and biocompatibility, depend on the state of the surface, modern methods of surface engineering are particularly useful. They include the deposition of layers with a matching chemical composition and structure. In terms of applications, the most suitable seem to be amorphous or nanocrystalline layers containing carbon, nitrogen, silicon and hydrogen. They combine the advantageous properties of silicon carbide SiC and silicon nitride Si₃N₄ and thus have a strong resistance to oxidation at high temperatures, high modulus of elasticity, low coefficient of friction and wear resistance. However, the silicon carbonitride compound is not thermodynamically stable under normal conditions and therefore must be obtained as a result of unconventional synthesis. One of these methods is chemical vapor deposition (CVD), including the most widely used plasma-assisted chemical vapor deposition (PACVD) techniques. The materials obtained, thanks to these techniques, have found and are still finding wider and wider application in many branches of industry and medicine.

Keywords: CVD, plasma, DLC layers, polymers, Ti alloy, Al alloy

1. Introduction

For several dozen years, scientists have been involved in obtaining diamond-like carbon (DLC) layers by various methods. Depending on the predominance of phenomena or the type of physical, chemical, or physicochemical interaction on the core or the substrate, it can be divided into six groups of methods: mechanical, thermomechanical, thermal, electrochemical, chemical, and physical [1]. Among them, plasma-assisted chemical vapor deposition (PACVD)
techniques are most commonly used. These methods, thanks to the activation of chemical processes in the gas phase, which is a low-temperature plasma, allow for obtaining layers at relatively low temperatures [2, 3].

The history of amorphous carbon nitride (a-C:N:H) layers originated in the 1990s of the last century, when Liu and Cohen [4], using numerical methods, suggested the stability of β-C$_3$N$_4$ crystal (Figure 1). According to them, this crystal would have a structure analogous to β-Si$_3$N$_4$, characterized by short bonds and high covalence (about 93%). According to the predictions of these authors, C$_3$N$_4$ should have a modulus of stiffness and hardness even greater than diamond. Attractive, predicted properties of this material have become the cause of intense research on the synthesis of this crystal. In most experiments, however, amorphous materials were obtained with maximum nitrogen consisting of up to 45%. Only in a small number of cases, evidence for the existence of C$_3$N$_4$ in crystalline form has been found. In works [5, 6], small crystals in an amorphous matrix were observed under a transmission electron microscope (TEM).

Failed attempts to synthesize crystalline C$_3$N$_4$ lead to an increased interest in amorphous carbon nitride in the form of layers. These layers, as it turned out, are characterized by high wear resistance and a low coefficient of friction and thus can become competitive to diamond-like carbon (DLC) layers, which are well known and used in various branches of technology and medicine. This fact makes the a-C:N:H layers the focus of many research centers in the world.

Pioneer, though unsuccessful, research in crystalline C$_3$N$_4$ production also resulted in the discovery of the new SiC$_x$N$_y$ silicon carbonitride compound, which combines the properties of silicon nitride, silicon carbide, and carbon nitride. Depending on the synthesis conditions and the precursors used, this compound may exist in both crystalline and amorphous forms [8, 9], and its chemical composition may change.

For example, at low temperatures, using precursors containing hydrogen in their composition, amorphous layers are formed in which this element occurs in their structure in a bonded form (SiC$_x$N$_y$(H)) [10, 11].

It is understood that the properties of these layers depend on their chemical composition and structure.

Figure 1. Computer model C3N4 [7].
Materials with this type of applied layers have found wide application in many branches of the industry (electronics, optics, aviation, shipbuilding, construction) and in medicine.

A more detailed discussion of these problems will be provided in this chapter.

2. CVD techniques

In CVD processes, the growth of the coating is limited by the rate of chemical reactions between the adsorbed gas molecules on the surface of the substrate. At low temperatures, the growth of the layers is limited by chemical reactions and at high temperatures by diffusion of active products to the surface.

The partition of CVD methods (Figure 2) can be carried out in terms of:

• Gas substrate type: halide (H) and organometallic (MO)
• Pressure: atmospheric (AP) and depressed (LP)

The later methods (LP CVD) are divided by the way in which the process is activated:

• Plasma (PA):
  ○ Glow discharge (DC)
  ○ Radio frequency (RF)
  ○ Microwaves (MW)

Figure 2. The partition of CVD methods [1].
Electrons (EA)
  ○ Thermoemission (HF)
  ○ Bunch (EA)

• Photons (PhA)

The main difference between conventional and plasma-activated CVD methods lies in the fact that, in the case of PACVD, the molecules are in a higher state of internal energy. Electric discharges of 2.45 GHz (microwaves) and 13.56 MHz (radio waves) are among the most useful methods of producing low-temperature plasma [12, 13].

Figure 3a shows the reactions occurring in the CVD process involving plasma. The presence of particles with an increased state of internal energy and ion bombardment on the surface of the substrate increases the surface diffusion rate and decreases the activation energy of chemical reactions leading to the formation of a coating. Layering takes place at a much lower temperature.

This raises the question of what can affect the design of coating technologies. This can be considered from two sides:

• The need to meet the requirements in relation to the physicochemical parameters of the surface of the workpiece.
• Compliance with the economic aspect.

For processes taking place under reduced pressure, aside from the choice of the method, the individual processing phases are of particular importance. An important role is also played by the type of intermediate layers and final obtained coatings and thus the technological parameters of each stage.

Temperature is one of the process parameters. If CVD processes are generated by plasma, the treatment can already be carried out at room temperature. This is related to the activation of chemical reactions in the gas phase by electrons accelerated in an electromagnetic field.

In that case of coating deposition, with time, subsequent stages of layer growth occur, which consequently form a continuous structure on the surface (Figure 3b).

In addition to the substrate temperature and the power of the plasma generator, the technological parameters related to the gas precursors themselves, i.e., their type and partial pressure, also have an influence on the structure and properties of the obtained coatings. Controlling these parameters also affects the microstructure of the resulting layers [14], which can be:

• Amorphous
• Fine grained
• Polycrystalline
2.1. The role of plasma

The commonly known definition of plasma is, according to Langmuir [15], partially or almost completely ionized gas, which is also the fourth state of matter (97% of the universe [16]). Initially, it was an object of interest only among physicists. However, application in materials technology was also quickly found.

Research into the improvement of physical properties, as well as physicochemical properties, such as wear and corrosion resistance of thin films and coatings, has somehow contributed to the use of plasma energy for obtaining materials in the form of layers and coatings on various types of surface substrates.

The reactor chamber is a kind of unloading pipe in which (under reduced pressure (about 10–80 Pa), the influence of electromagnetic waves is present) gas ionizing energy is supplied with a strictly defined and controlled flow rate [17]. The results of this process are also:

- Reactions between dissociated molecules that may be neutral or ionized.
- Increasing the temperature of the substrate, ions and neutral molecules with high kinetic energy falling on its surface can be additionally supported by the use of heating elements in the system.
- Transport and adsorption processes of atoms and ions—under conditions of temperature gradient and concentration of components on the surface of the substrate—and their transport toward the core of the material.
- Coating growth—heterogeneous reactions in thermodynamically privileged places on the surface (active sites).

2.2. Synergism in coating technology

The concept of synergism is used in various fields of science. As a technique, it is usually referred to as the interaction of more than one factor for the final effect obtained (improvement of a given physicochemical property or obtaining a completely new functionality).

This definition is also reflected in surface technology. However, it is assumed here every time that the obtained effects are due to the influence of many factors [1]. In this case the term synergism refers here to the usable properties of the modified surface. This action is achieved by:

- Choosing the right method for treating the substrate surface.
- Selecting chemical and phase composition of coatings.
- Using transitional layers (so-called interlayers), this has a significant impact on adhesion of the obtained coatings to the surface.

Therefore, we can say that it is necessary to design technology in many experimental works that ensures optimal material parameters that are maximally beneficial for the given application (both the properties of the coatings obtained and their adhesion to the surface).
Figure 3. (a) Scheme of reactions occurring in the PACVD process. (b) Scheme of processes occurring in the plasma reactor with the stages of coating deposition. (according to Kyziol's work [18]).
3. Techniques for obtaining DLC layers

3.1. Overview of techniques for receiving thin layers

Techniques for obtaining DLC layers can be divided into two groups [19]. The criterion for this division is the type of precursor used in the process.

The first group brings together methods in which the precursor is solid carbon:

• Atomizing a carbon electrode with a single-ion beam (sputtering beam)—spraying a carbon disk with a single argon ion beam with energy from 0.5 to a few keV; the carbon atoms removed from the electrode after getting bombarded with gas ions are ionized themselves and deposited on the appropriate surface, forming an amorphous layer without the presence of hydrogen [20] (Figure 4a).

• Atomization of the carbon electrode with a double-ion beam (dual-ion beam sputtering)—introducing of an additional source of hydrogen or hydrocarbon ions with 1 keV energy; their task is to bombard the growing carbon layer, after which carbon ions react with hydrogen or hydrocarbon to form a hard layer with a quasi-amorphous structure (Figure 4b).

The second technique includes methods in which saturated or unsaturated hydrocarbon gas is used as a precursor (acetylene, benzene, butane, cyclohexane, ethane, ethylene, hexane, isopropene, methane, pentane, propane, and propylene). This group of methods consists primarily of plasma-assisted chemical vapor deposition (PACVD) technologies. These include methods such as:

• MW CVD (microwave chemical vapor deposition)
• RF CVD (radio-frequency chemical vapor deposition)
• DC CVD (direct-current chemical vapor deposition)
• Arc discharge method

Currently, the methods included in the second group receive the most interest and are subject to continuous and intensive modernization.

There is also a method that cannot be assigned to the abovementioned groups in any way. It is a method of laser graphite ablation involving the evaporation of a graphite target using a laser.

Due to the circumstances (CVD methods described above), I will discuss this second group in more detail, that is, obtaining DLC layers using PA CVD methods.
3.2. PA CVD and DLC layers

In the twenty-first century, most research pertains to the technology of DLC coatings, including the modification of these other atoms (in medical applications N, Si, Ti, O, F, and Ag) [22–30]. For their synthesis, the most common method is chemical vapor deposition.

The discussed layers, due to their number of interesting properties (Table 1), are used in many branches of the industry.

In “Introduction,” I already mentioned pioneer studies concerning these layers. Up to now, however, carbon nitride has not been obtained in a crystalline form with stoichiometric or a very similar atomic ratio, and a series of works carried out in this area led to obtaining carbon layers subsidized with nitrogen atoms (N-DLC) [38–40], silicon (Si-DLC) [25, 30, 41–43], or more complex, in terms of chemical composition, SiCN:H structures [44, 45].

DLC coatings are largely amorphous, in which carbon is present in the sp² and sp³ hybridizations. The clusters of atoms have a structure typical for graphite, somehow immersed in an amorphous matrix, which consist of carbon atoms [46]. The general classification of the discussed coatings is as follows [31, 47]:

- Hydrogenated structures
- Nonhydrogenated structures

In both cases, they can be doped with both metals and nonmetals. Many scientists have been investigating layers with various types of atoms [48–54].

The addition of Ti, W or Si, and N improves adhesion to the substrate, and according to Galvan et al. [49], they decrease the level of their own stresses in the DLC structure. In turn,
Dwivedi et al. [50] confirmed that nitrogen, as an additive (N-DLC), causes changes in the morphology of coatings both on a nanometric and micrometric scale, which favors the binding of sp² hybridization clusters. The improvement of anticorrosive properties by doping with silicon atoms was noticed by Kim et al. [51], even with the Si contribution not exceeding 2% at.

In addition to the abovementioned influence, Si-DLC coatings also exhibit a more favorable hardness—hindering the formation of sp² moieties for the contribution of amorphous structure to sp³ hybridization (e.g., a decrease in hardness from 23.1 to 13.7 GPa, with an increase in Si content from zero to 19.73% at [48]) [54] in comparison to, among others, Si/N-DLC coatings, high growth rate in the production process [52], good oxidation resistance, and low value of the coefficient of friction [53]. Thanks to these properties, these coatings have a wide range of applications in the automotive, aerospace, and shipbuilding industries.

Therefore, it can be argued that for the design of technology based on chemical reactions, in short CVD, the key step is the optimization of the structure of the obtained layers and the related functional properties of the materials. The goal of this approach to the discussed issue is to ensure the best possible adjustment of the surface treatment parameters in terms of the use of a given structural element.

### 3.3. The influence of PA CVD process parameters on the structure of N-DLC coatings

Proper selection of the technological process parameters for coating production is one of the key factors that improves their synergism on various types of substrates. In the case of chemical plasma vapor deposition (PA CVD (plasma-assisted chemical vapor deposition)) processes, this is particularly important. The keys to the construction and physicochemical properties of a given surface are:

- Duration of the process
- Temperature in the reactor and at the surface itself
- Pressure in the reaction chamber

| Type of material | sp³ (%) | H (%) | Density (g/cm³) | Hardness (GPa) |
|------------------|---------|-------|---------------|--------------|
| Diamond          | 100     | 0     | 3.5           | 100          |
| Graphite         | 0       | 0     | 2.3           |              |
| a-C:H (soft)     | 60      | 40–50 | 1.2–1.6       | <10          |
| a-C:H (hard)     | 40      | 30–40 | 1.6–2.2       | 10–20        |
| ta-C:H           | 70      | 30    | 2.4           | 50           |
| N-DLC            | 14–21   | About 36 | 1.9–2.4   | 22–28        |

Table 1. Selected properties of carbonaceous materials, including DLC and N-DLC layers (based on [18, 31–37]).
- Power of the plasma generator
- Flow rate and type of gas precursor
- Condition and type of surface

In this respect, the technology is extremely difficult to develop. The processes occurring during deposition largely take place away from thermodynamic equilibrium. Summing up the design and development of this technology most often requires a number of experimental studies.

The research conducted by our team on the impact of gas mixture composition, process temperature, plasma generator power, and reactor pressure on the growth rate of N-DLC structures was a valuable guideline for its design. With regard to nitrogen-rich DLC layers, it can be concluded that the growth rate of these structures decreases with increasing temperature and as the proportion of N\textsubscript{2} in the gas mixture increases. This can be counteracted by increasing the power of the plasma generator and the pressure of the gaseous reactants in the working chamber. It is worth noting that for each type of layers, including N-DLC, limit values of individual parameters are defined, at which the aforementioned layers are thermodynamically stable [55].

4. DLC layers on different substrates

Adhering strictly to the guidelines presented in this chapter, in designing technology for modification of all kinds of materials, the parameters for individual stages of machining were selected so as to minimize the possibility of ionic etching of the resulting coatings to ensure maximum speed of the deposition process.

Figure 5 schematically represents the structure of the layers on Ti6Al4V.

The following subsections present examples of DLC layer deposition processes on several types of substrates, and the parameters of which are presented in Table 2.

4.1. Titanium and aluminum alloys

The diffusion processes are important for the treatment technology performed on these Ti- and Al-based alloys, which consequently leads to the formation of phases that strengthen the surface layer. In the case when their surface is nitrided, this process is usually carried out in N\textsubscript{2} [57, 58], N\textsubscript{2}-H\textsubscript{2} [59, 60], and NH\textsubscript{3}-Ar atmospheres [61, 62]. While the role of nitrogen is obvious, the effect of hydrogen has been explained in various ways. For example, Matsumoto [63] believes that H\textsubscript{2} reduces the reaction rate, while Renevier et al. [64] assume that the addition of H\textsubscript{2} to N\textsubscript{2} is not important. On the other hand, Hudis [65] demonstrates that the addition of hydrogen ensures a more effective cleaning of the surface, which promotes the nitriding process. In addition, studies conducted by Negm [66] have confirmed that the replacement of hydrogen with argon or another inert gas reduces the thickness of diffusion layers and the hardness of the treated surface.
Our team conducted a lot of researches on DLC layers deposited on substrates [56]. The results for the Ti Grade 2 (after plasma processes) obtained from the biological and corrosion tests suggest that titanium with the plasmochemically modified surface did not cause severe cytotoxicity against MG63 cells and improves corrosion properties. Similarly, beneficial results of the transfer of stresses between the substrate and the coating after using the surface modification process with nitrogen or silicon ions were obtained in the work on the modification of aluminum alloys [43, 67, 68]. For example, Lifang et al. [69] clearly indicate that obtaining an intermediate layer, at the Al-Cu-Mg-DLC alloy boundary, decisively influences, inter alia, the hardness of the surface exposed to working conditions. The various intermediate layers obtained by these authors, under different conditions of plasma ion implantation (PBII (plasma-based ion implantation)), lead to changes in the degree of surface hardening (in the range 17–22 GPa) and the extent of the alloy’s strengthening (800–1350 nm).

### Table 2. Details for plasma modification including carbon-based coating deposition [56].

| Substrate       | Type of plasmochemical process | Technological parameters |
|-----------------|--------------------------------|--------------------------|
|                 |                                | Gas/flow (sccm)          | $P_{RF/MW}$ (W) | $T_s$ (°C) | p (Tr) | t (min) |
| Ti Grade 2      | SiCH                           | Ar/225; CH$_4$/25; SiH$_4$/3 | $P_{RF}$ 400 | 600 | 0.3 | 30 |
|                 | SiNH                           | Ar/225; NH$_3$/150; SiH$_4$/3 | $P_{RF}$ 400 | 600 | 0.3 | 30 |
|                 | SiCNH                          | Ar/225; NH$_3$/130; CH$_4$/20; SiH$_4$/3 | $P_{RF}$ 400 | 600 | 0.3 | 30 |
| Al-Zn alloy     | N$^+$ ion                      | N$_2$/90; H$_2$/30        | $P_{RF}$ 100 | 350 | 0.7 | 120 |
| Polyetherketone | CNH                            | Ar/80; SiH$_4}$/8; CH$_4$/8 | $P_{RF}$ 50  | 400 | 0.4 | 8   |
|                 | Si-DLC                         | Ar/75; N$_2$/85; CH$_4$/10 | $P_{RF}$ 80  | 24  | 0.4 | 30 |
|                 | SiCNH                          | Ar/75; N$_2$/25; CH$_4$/104; SiH$_4$/3 | $P_{RF}$ 80  | 24  | 0.4 | 30 |

$P_{RF/MW}$ radio-frequency or microwave generator power; $T_s$, substrate temperature; p, pressure in the reactor; t, time of process deposition.

Figure 5. The scheme of DLC layer structure.
However, with respect to the structure of the coatings themselves, for example, Wang et al. [70] and Ikeyama et al. [71] confirmed that the addition of Si to the DLC structure improves the adhesion of the coating to the substrate and reduces the level of internal stresses in its structure. In turn, subsidizing the DLC structure with nitrogen atoms results in a decrease in the coefficient of friction [72].

In the case of our team’s research on modification of the Al-Zn alloy (after modification of nitrogen ions and deposition of SiCH layers), an improvement in hardness (up to 8 GPa), Young’s modulus (up to 6 GPa), and surface smoothness (surface roughness parameter) were observed.

**Figure 6** presents photos of modified metallic materials.

![Images of different substrates with DLC layers: (a) Ti Grade 2, (b) Ti6Al4V, (c) Ti-Al, and (d) Al-Zn.](image)

4.2. Polymers

During the last decade, PEEK has generated much interest thanks to its thermoplastic properties, chemical resistance, high-temperature stability, and biocompatibility [73, 74]. It has been considered as a suitable material replacing metals in biomedical implants and as a matrix of carbon fiber composites [75, 76]. However, it also has disadvantages, namely, hydrophobicity and low surface free energy, resulting in poor adhesive properties. In order to improve the properties of PEEK, we modified the samples with ion etching and deposited layers a-CN:H/a-SiCN:H by using RFCVD [56].

**Figure 7** presents photo of modified PEEK.
4.3. Austenitic-ferritic steel

In this respect, especially in the case of DLC coatings obtained on metallic substrates (e.g., steel), this process is preceded by interlayer deposition. A transitional layer often containing silicon [43] significantly improves the adhesion of the specific coating to metal alloys and at the same time prevents an unfavorable phenomenon, which in this case is the precipitation of iron-carbon phases.

In the work of Stypuła, et al. [77] it was found that nitriding austenitic-ferritic steel (duplex) using radio-frequency plasma, under low-pressure and low-temperature conditions \((p = 0.7Tr, T = 573 K)\) improves the passivation parameters and corrosion resistance of the \(\text{LOOH21N7MC}\) alloy. This increase in corrosion resistance is associated with high nitrogen content (~21%), with the oxide-nitride structure of the nitrided outer layer, as well as a high degree of surface enrichment in the silicon in the form of a nitride.

Brylewski et al. [78] used PACVD to obtain a silicon carbonitride layer with a defined desired chemical composition on Crofer 22APU steel, both without and after prior nitriding. It was determined that nitriding has a positive influence on the microhardness and elasticity modulus of the investigated \(\text{SiC}_x\text{N}_y\text{(H)}\) layer. High-temperature oxidation studies performed on the samples indicate that prior nitriding in plasmochemical conditions results in improved corrosion resistance of the Crofer 22APU steel with the deposited \(\text{SiC}_x\text{N}_y\text{(H)}\) layer. From these studies it can be concluded that the deposition of the silicon carbonitride layer preceded by nitriding can be successfully used to obtain materials with potential applications as interconnects in planar-type intermediate-temperature solid oxide fuel cells.

5. Application

Thanks to their properties, such modified materials have found a fairly wide application in several branches of the industry, construction, and medicine. The first group includes, among others, car industry, aviation, shipbuilding, electronics. The second one is mainly photovoltaics, various types of constructions, machines, and parts of construction machines. In contrast, the
third group consists of a wide range of applications, from bone implants to medical instruments and veterinary. A separate group includes sports, especially golf, sailing, or canoeing.

Figure 8 presents photos of examples of applications for modified materials.

Author details

Marta Januś

Address all correspondence to: martaj@agh.edu.pl

AGH–University of Science and Technology, Faculty of Materials Science and Ceramics, Krakow, Poland

References

[1] Burakowski T. Rozważania o synergizmie w inżynierii powierzchni [Considerations on Synergism in Surface Engineering]. Radom: Wydawnictwo Politechniki Radomskiej; 2004

[2] Musil J, Vlček J, Růžička M. Recent progress in plasma nitriding. Vacuum. 2000;59:940-951

[3] Chu PK, Chen JY, Wang LP, Huang N. Materials science and engineering reports: A review. Journal. 2002;36:143-206

[4] Liu AY, Cohen ML. Structural properties and electronic structure of low-compressibility materials: Beta-Si₃N₄ and hypothetical beta-C₃N₄. Physical Review. 1990;B41:10727
[5] Matsumoto O, Kotaki T, Sikano H. Synthesis of carbon nitride in plasma arc. Journal of the Electrochemical Society. 1994;141:L16-L18

[6] Yu KM, Cohen ML, Haller EE. Observation of crystalline \( \text{C}_3\text{N}_4 \). Physical Review. 1994;B49:5034-5037

[7] Xianhui B, Zheng N, Li Y, Feng P. Templated assembly of sulfide nanoclusters into cubic-C\( _3\text{N}_4 \) type framework. Journal of the American Chemical Society. 2003;125(20):6024-6025

[8] Chen LC, Luang JY. Crystalline silicon carbon nitride: A wide band gap semiconductor. Applied Physics Letters. 1998;72(19):2463-2465

[9] Chen LC, Wei SL. Crystalline SiCN: A hard material rivals to cubic BN. Thin Solid Films. 1999;355-356:112-116

[10] Błaszczyk-Lezak I, Wróbel AM, Bieliński DM. Remote hydrogen microwave plasma chemical vapor deposition of silicon carbonitride films from a (dimethylamino) dimethyilsilane precursor: Compositional and structural dependencies of film properties. Diamond and Related Materials. 2006;15:1650-1658

[11] Fainer NI, Maximovsky EA, Rumyantsev YM, Kosinova ML, Kuznetsov FA. Composition and structure of silicon carbonitride layers grown on Si(100)/(Fe, N, Co) substrates. Nuclear Instruments and Methods in Physics Research A. 2001;470:193-197

[12] Norm ISO 5832/3-1978 (E). Implants for surgery—Metallic materials wrought titanium 6-aluminium 4-vanadium alloy. ISO; 1978

[13] Norm ASTM F136-98. Standard specification for wrought titanium-6aluminum-4vanadium ELI. USA; 1998

[14] Somiya S, Goto T. Handbook of Advanced Ceramics. Elsevier; 2013

[15] Langmuir I. Oscillations in ionized gases. Physical Review. 1928;14:627-637

[16] Merche D, Vandencasteele N, Reniers F. Atmospheric plasmas for thin film deposition: A critical review. Thin Solid Films. 2012;520:4219-4236

[17] Lebrun JP. Applications of low-temperature surface hardening of stainless steels. Thermochemical Surface Engineering of Steels. Elsevier; 2015. pp. 633-647

[18] Kyziol K. Funkcjonalne powłoki otrzywmywane w warunkach plazmochemicznych [Functional coatings obtained under plasmochemical conditions]. Ceramics. 2016;123

[19] Spear KE, Dismukes JP. Synthetic Diamond: Emerging CVD Science and Technology. USA: John Wiley & Sons, Inc.; 1994

[20] Paiva OC, Santos JD, Reis RL. An electrochemical study on anodised Ti-6Al-4V aiming at improving its biomedical performance. In: Proceedings of the Symposium on Compatibility of Biomedical Implants. Vol. 94-15. p. 145

[21] Anderson L-P. A review of recent work on hard i-C films. Thin Solid Films. 1981;86:193
[22] Kluba A, Bociąga D, Dudek M. Hydrogenated amorphous carbon films deposited on 316L stainless steel. Diamond and Related Materials. 2010;19:533-536

[23] Tétard F, Djemia P, Angleraud B, Mubumbila N, Tessier PY. Surface and bulk characterizations of CNx thin films made by r.f. magnetron sputtering. Surface and Coatings Technology. 2002;151-152:184-188

[24] Zhang P, Tay BK, Yu GQ, Lau SP, Fu YQ. Surface energy of metal containing amorphous carbon films deposited by filtered cathodic vacuum arc. Diamond and Related Materials. 2004;13:459-464

[25] Bociąga D, Kamińska M, Sobczyk-Guzenda A, Jastrzębski K, Świątek L, Olejnik A. Surface properties and biological behaviour of Si-DLC coatings fabricated by a multi-target DC-RF magnetron sputtering method for medical applications. Diamond and Related Materials. 2016;67:41-50

[26] Bociąga D, Komorowski P, Batory D, Szymański W, Olejnik A, Jastrzębski K, Jakubowski W. Silver-doped nanocomposite carbon coatings (Ag-DLC) for biomedical applications—Physiochemical and biological evaluation. Applied Surface Science. 2015;355:388-397

[27] Bociąga D, Jakubowski W, Komorowski P, Sobczyk-Guzenda A, Jędrzejczak A, Batory D, Olejnik A. Surface characterization and biological evaluation of silverincorporated DLC coatings fabricated by hybrid RF PACVD/MS method. Materials Science and Engineering C. 2016;63:462-474

[28] Batory D, Jędrzejczak A, Kaczorowski W, Szymański W, Kołodziejczyk L, Clapa M, Niedzielski P. Influence of the process parameters on the characteristics of silicon-incorporated a-C:H:SiOx coatings. Surface and Coatings Technology. 2015;271:112-118

[29] Batory D, Jędrzejczak A, Szymański W, Niedzielski P, Fijałkowski M, Louda P, Kotela I, Hromadka M, Musil J. Mechanical characterization of a-C:H:SiOx coatings synthesized using radio-frequency plasma-assisted chemical vapor deposition method. Thin Solid Films. 2015;590:299-305

[30] Szmidt J, Beck RB, Lisik Z, Mitura S, Sokółowska A. State of the silicon-DLC layer interface produced by plasma methods. Diamond and Related Materials. 1996;5:1204-1209

[31] Robertson J. Diamond-like amorphous carbon. Materials Science & Engineering R: Reports. 2002;37:129-281

[32] Field JE, editor. The Properties of Natural and Synthetic Diamond. London: Academic Press; 1992

[33] Cahn RW. Physics of graphite. Journal of Nuclear Materials. 1983;114:116-116

[34] Koidl P, Wild C, Dischler B, Wagner J, Ramsteiner M. Plasma deposition, properties and structure of amorphous hydrogenated carbon films. Materials Science Forum. 1990;52-53:41-70
[35] Weiler M, Sattel S, Jung K, Ehrhardt H, Veerasamy VS, Robertson J. Highly tetrahedral, diamond-like amorphous hydrogenated carbon prepared from a plasma beam source. Applied Physics Letters. 1994;64:2797-2799

[36] Donnet C. Recent progress on the tribology of doped diamond-like and carbon alloy coatings: A review. Surface and Coatings Technology. 1998;100-101:180-186

[37] Murata Y, Choo CK, Ono H, Nagai Y, Tanaka K. Characterization of N-doped DLC thin films prepared by hydrocarbons pyrolysis method. Materials Today: Proceedings. 2016;3:197-202

[38] Motta EF, Pereyra I. Amorphous hydrogenated carbon-nitride films prepared by RF-PECVD in methane-nitrogen atmospheres. Journal of Non-Crystalline Solids. 2004;338-340:525-529

[39] Neuville S, Matthews A. A perspective on the optimisation of hard carbon and related coatings for engineering applications. Thin Solid Films. 2007;515:6619-6653

[40] Yang P, Huang N, Leng YX, Chen JY, Wang J, Sun H, Wan GJ, Zhao AS. Wettability and blood-compatibility of a-C:N:H films deposited by PIII-D. Surface and Coatings Technology. 2010;204:3039-3042

[41] Soum-Glaude A, Thomas L, Dollet A, Ségur P, Bordage MC. Argon/tetramethysilane PECVD: From process diagnostic and modeling to a-Si:C:H hard coating composition. Diamond and Related Materials. 2007;16:1259-1263

[42] Iseki T, Mori H, Hasegawa H, Tachikawa H, Nakanishi K. Structural analysis of Si-containing diamond-like carbon. Diamond and Related Materials. 2006;15:1004-1010

[43] Cemin F, Boeira CD, Figueroa CA. On the understanding of the silicon-containing adhesion interlayer in DLC deposited on steel. Tribology International. 2016;94:464-469

[44] Peter S, Bernütz S, Berg S, Richter F. FTIR analysis of a-SiCN:H films deposited by PECVD. Vacuum. 2013;98:81-87

[45] Kafrouni W, Rouessac V, Julbe A, Durand J. Synthesis of PECVD a-SiCxNy:H membranes as molecular sieves for small gas separation. Journal of Membrane Science. 2009;329:130-137

[46] Spencer EG, Schmidt PH, Joy DC, Sansalone FJ. Ion beam deposited polycrystalline diamond-like films. Applied Physics Letters. 1976;29:118-120

[47] Lifshitz Y. Diamond-like carbon—Present status. Diamond and Related Materials. 1999;8:1659-1676

[48] Bogdanowicz R. Advancements in diamond-like carbon coatings. Handbook of Nanoceramic and Nanocomposite Coatings and Materials. Elsevier; 2015. pp. 183-200

[49] Galvan D, Pei YT, De Hosson JTM. Influence of deposition parameters on the structure and mechanical properties of nanocomposite coatings. Surface and Coatings Technology. 2006;201:590-598
[50] Dwivedi N, Kumar S, Malik HK, Rauthan CMS, Panwar OS. Influence of bonding environment on nano-mechanical properties of nitrogen containing hydrogenated amorphous carbon thin films. Materials Chemistry and Physics. 2011;130:775-785

[51] Kim H-G, Ahn S-H, Kim J-G, Park SJ, Lee K-R. Effect of Si-incorporation on wear-corrosion properties of diamond-like carbon films. Thin Solid Films. 2005;482:299-304

[52] Jiang L, Chen X, Wang X, Xu L, Stubhan F, Merkel K-H. a-SiCx:H films deposited by plasma-enhanced chemical vapor deposition at low temperature used for moisture and corrosion resistant applications. Thin Solid Films. 1999;352:97-101

[53] Damasceno JC, Camargo SS, Freire FL, Carius R. Deposition of Si-DLC films with high hardness, low stress and high deposition rates. Surface and Coatings Technology. 2000;133-134:247-252

[54] Tang J, Wang Y. Characterization of DLC-Si films prepared by RF-PECVD. In: Optoelectronics and Microelectronics (ICOM). 2012. pp. 431-433

[55] Kyzioł K, Jonas S, Tkacz-Śmiech K, Marszalek K. A role of parameters in RF PA CVD technology of a-C:N:H layers. Vacuum. 2008;82:998-1002

[56] Januś M, Kluska S, Kyzioł K, Jonas S. Plasma assisted chemical vapour deposition—Technical design of functional coatings. Polish Academy of Sciences, Committee of Metallurgy, Institute of Metallurgy and Materials Science, Archives of Metallurgy and Materials. 2015;60(2):909-914

[57] Gredelj S, Gerson AR, Kumar S, McIntyre NS. Plasma nitriding and in situ characterisation of aluminium. Applied Surface Science. 2002;199:234-247

[58] Quast M, Mayr P, Stock HR. Plasma monitoring of plasma-assisted nitriding of aluminium alloys. Surface and Coatings Technology. 1999;120-121:244-249

[59] Mubarak Ali M, Ganesh Sundara Raman S, Pathak SD, Gnanamoorthy R. Influence of plasma nitriding on fretting wear behaviour of Ti–6Al–4V. Tribology International. 2010;43:152-160

[60] Vissutipitukul P, Aizawa T. Wear of plasma-nitrided aluminum alloys. Wear. 2005;259:482-489

[61] Wang PW, Sui S, Wang W, Durrer W. Aluminum nitride and alumina composite film fabricated by DC plasma processes. Thin Solid Films. 1997;295:142-146

[62] Avni R, Spalvins T. Nitriding mechanisms in Ar-N2, Ar-N2-H2 and Ar-NH3 mixtures in D.C. Glow discharges at low pressures (less than 10 Torr). Materials Science and Engineering. 1987;95:237-246

[63] Matsumoto O. Nitriding reaction of metals under plasma conditions. In: Proceedings of the International Ion Engineering Congress ISIAT’83, Kyoto; 1983. pp. 1379-1390

[64] Renevier N, Czerwiec T, Collignon P, Michel H. Diagnostic of arc discharges for plasma nitriding by optical emission spectroscopy. Surface and Coatings Technology. 1998;98:1400-1405
65] Hudis M. Study of ion nitriding. Journal of Applied Physics. 1973;44:1489-1496

66] Negm NZ. A study on rf plasma nitriding at a constant power in different H$_2$–N$_2$ mixtures at different temperatures. Materials Science and Engineering B. 2006;129:207-210

67] Liao JX, Xia LF, Sun MR, Liu WM, Xu T, Xue QJ. The tribological properties of a gradient layer prepared by plasma-based ion implantation on 2024 aluminum alloy. Wear. 2004;256:840-845

68] Liao JX, Xia LF, Sun MR, Liu WM, Xu T, Yang CR, Chen HW, Fu CL, Leng WJ. Structural characteristics of 2024 aluminum alloy plasma-based ion implanted with nitrogen then titanium. Applied Surface Science. 2005;240:71-76

69] Lifang X, Zhaohui Y, Jiaxuan L. Effects of intermediate layers on the tribological behavior of DLC coated 2024 aluminum alloy. Wear. 2004;257:599-605

70] Wang J, Pu J, Zhang G, Wang L. Tailoring the structure and property of silicon-doped diamond-like carbon films by controlling the silicon content. Surface and Coatings Technology. 2013;235:326-332

71] Ikeyama M, Nakao S, Miyagawa Y, Miyagawa S. Effects of Si content in DLC films on their friction and wear properties. Surface and Coatings Technology. 2005;191:38-42

72] Yan X, Xu T, Chen G, Yang S, Liu H. Study of structure, tribological properties and growth mechanism of DLC and nitrogen-doped DLC films deposited by electrochemical technique. Applied Surface Science. 2004;236:328-335

73] Oehr C. Plasma surface modification of polymers for biomedical use, Nuclear instruments and methods. In: Physics Research Section B: Beam Interactions with Materials and Atoms. Vol. 208. 2003. pp. 40-47

74] Kurtz SM, Devine JN. PEEK biomaterials in trauma, orthopedic, and spinal implants. Biomaterials. 2007;28:4845-4869

75] Briem D, Strametz S, Schroeder K, Meenen NM, Lehmann W, Linhart W, Ohl A, Rueger JM. Journal of Materials Science: Materials in Medicine. 2005;16:671-677

76] Kurtz SM. Applications of polyaryletheretherketone in spinal implants: Fusion and nations preservation. PEEK Biomaterials Handbook. William Andrew Publishing; 2011. pp. 201-220. Chapter 13

77] Stypuła B, Stepuch-Galik A, Kowalski K, Januś M, Bernasik A. Korozja wysokostopowego staliwia azotowanego plazmowo [Corrosion of plasma nitried cast stainless steel]. Ochrona przed Korozją. 2005;48(11s/A):66-71. ISSN: 0473-7733

78] Januś M, Kluska S, Bobruk M, Brylewski T, Jastrzębski W, Zimowski S, Grzesik Z. Effect of plasma-assisted CVD surface modification of Crofer 22APU steel on its selected physicochemical properties. Ochrona przed Korozją. 2015;58(11):418-422. ISSN: 0473-7733
