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DLC Layers Created Using CVD Techniques and Their Application

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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 -C₃N₄ crystal (**Figure 1**). According to them, this crystal would have a structure analogous to β -Si₃N₄, characterized by short bonds and high covalence (about 93%). According to the predictions of these authors, C₃N₄ 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 C₃N₄ 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 C₃N₄ 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 C₃N₄ production also resulted in the discovery of the new SiC_xN_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_xN_y(H)) [10, 11].

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

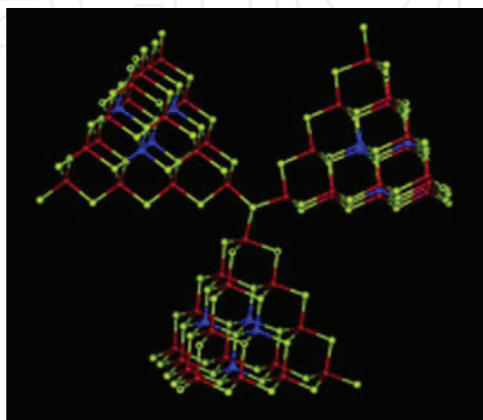


Figure 1. Computer model C₃N₄ [7].

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)

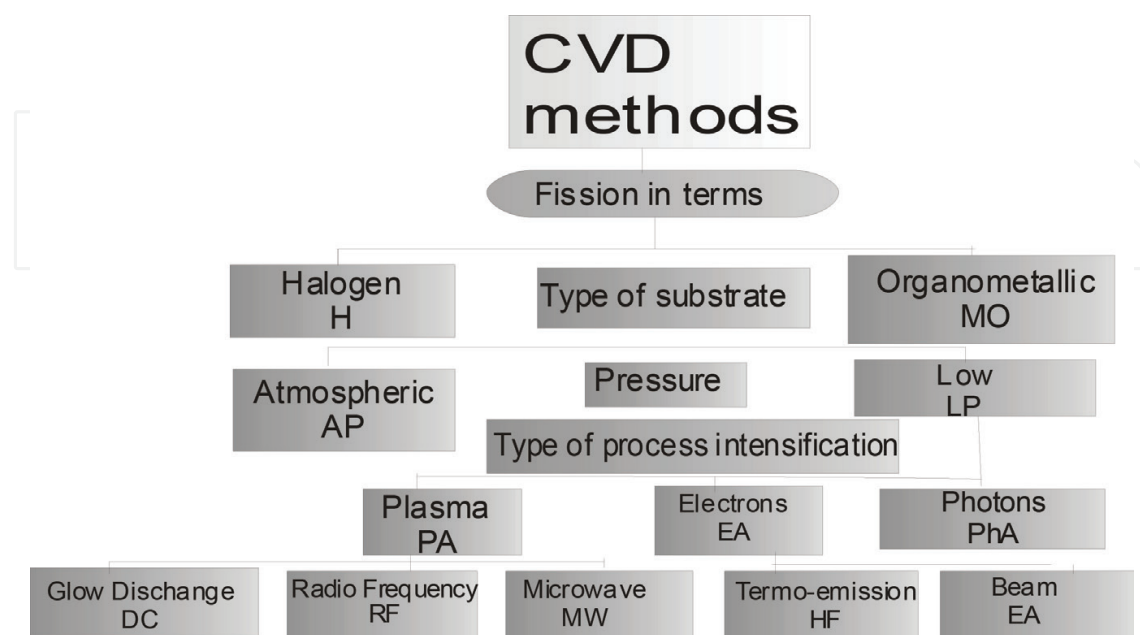


Figure 2. The partition of CVD methods [1].

- 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).

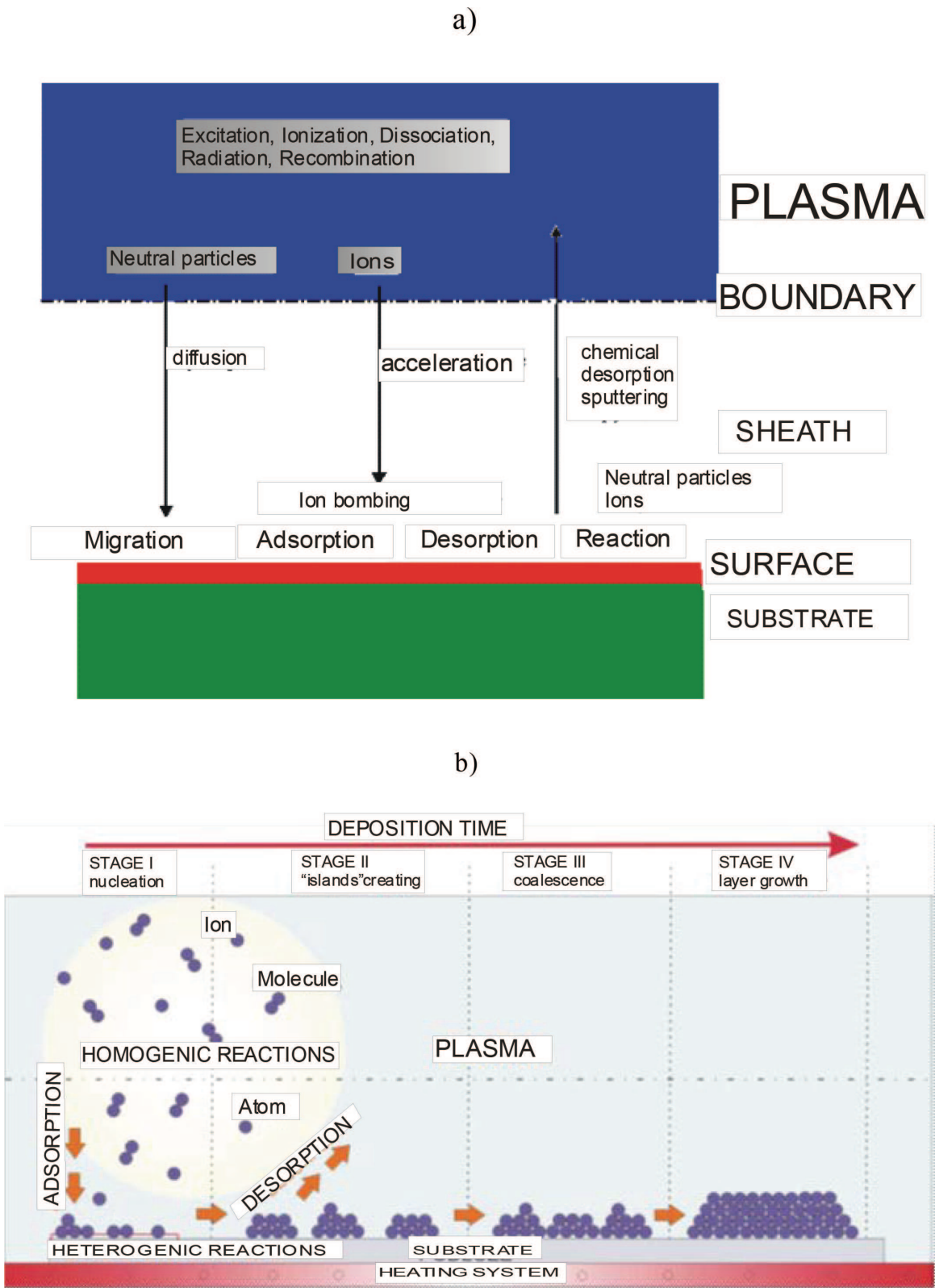


Figure 3. (a) Scheme of reactions occurring in the PACVD process. (b) Scheme of processes occurring in the plasma reactor with the stages of coating deposition. (according to Kyziol’s work [18]).

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, isopropane, 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.

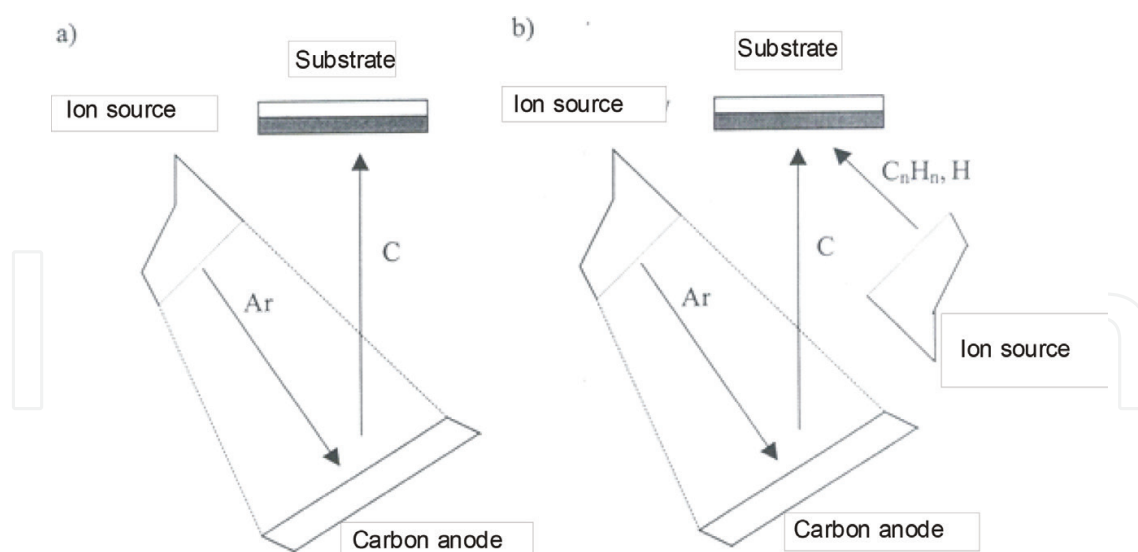


Figure 4. Scheme of systems for deposition by ion spraying: (a) single ion beam, (b) dual ion beam [21].

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 sp^2 and sp^3 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,

Type of material	sp ³ (%)	H (%)	Density (g/cm ³)	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]).

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

- 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_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_2 [57, 58], N_2 - H_2 [59, 60], and NH_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_2 reduces the reaction rate, while Renevier et al. [64] assume that the addition of H_2 to N_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.

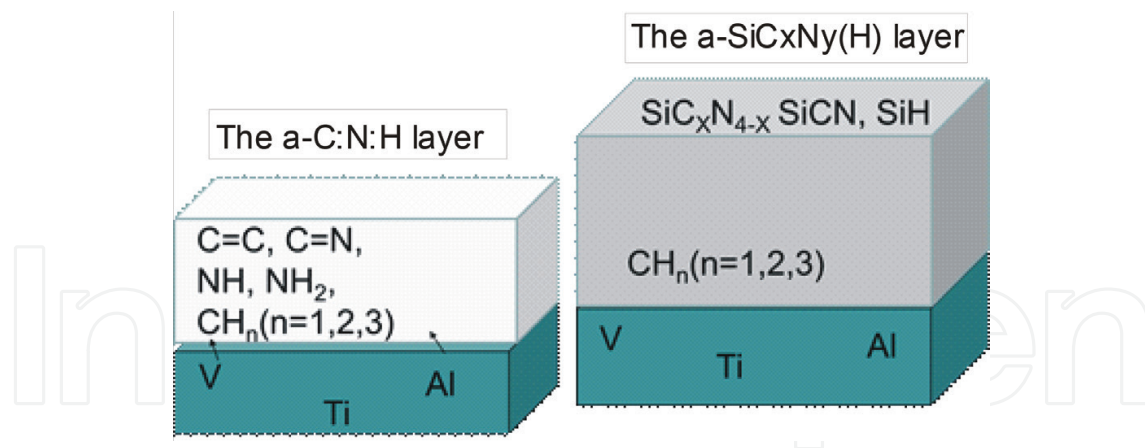


Figure 5. The scheme of DLC layer structure.

Substrate	Type of plasmochemical process	Technological parameters				
		Gas/flow (sccm)	$P_{RF/MW}$ (W)	T_s (°C)	p (Tr)	t (min)
Ti Grade2	SiCH	Ar/225; CH_4 /25; SiH_4 /3	P_{MW} 400	600	0.3	30
	SiNH	Ar/225; NH_3 /150; SiH_4 /3	P_{MW} 400	600	0.3	30
	SiCNH	Ar/225; NH_3 /130; CH_4 /20; SiH_4 /3	P_{MW} 400	600	0.3	30
Al-Zn alloy	N^+ ion	N_2 /90; H_2 /30	P_{RF} 100	350	0.7	120
	Si-DLC	Ar/80; SiH_4 /8; CH_4 /8	P_{RF} 50	400	0.4	8
Polyetherketone	CNH	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.

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

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).

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.

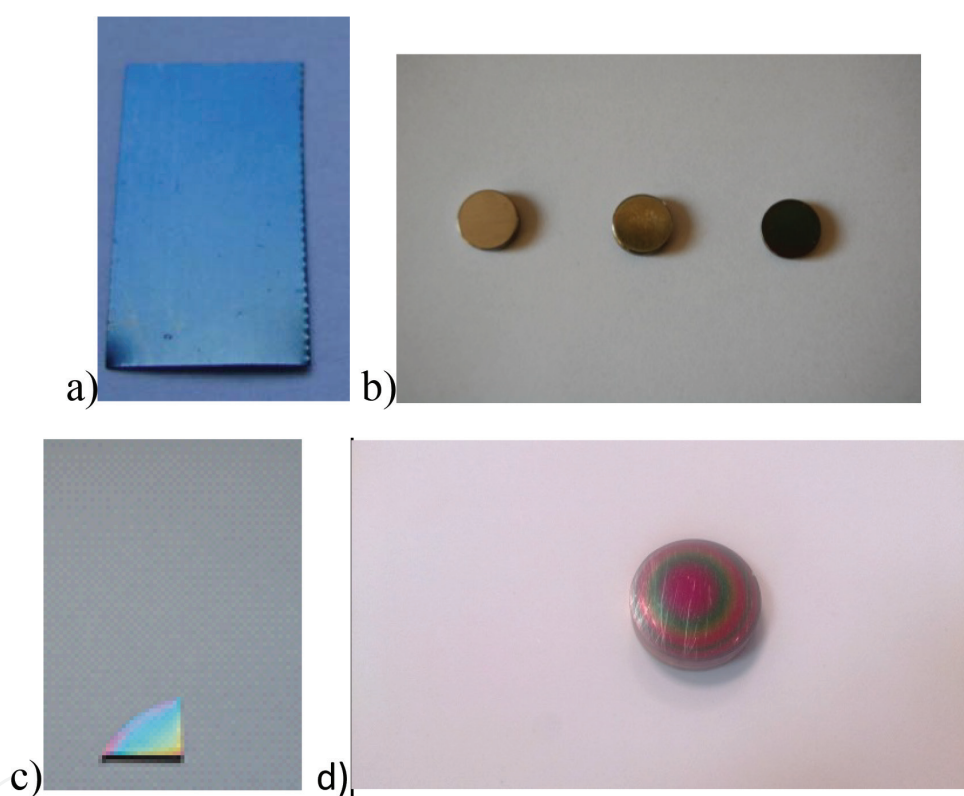


Figure 6. Images of different substrates with DLC layers: (a) Ti Grade 2, (b) Ti6Al4V, (c) Ti-Al, and (d) Al-Zn.

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.

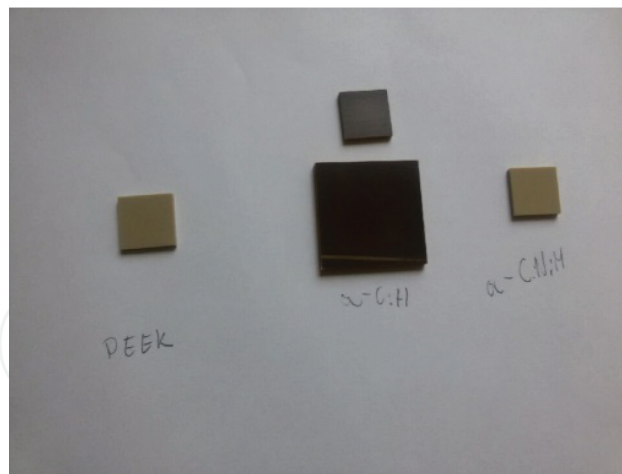


Figure 7. Image of PEEK with DLC layers.

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 ($p = 0.7 \text{ Tr}$, $T = 573 \text{ K}$) improves the passivation parameters and corrosion resistance of the LOOH21N7MC alloy. This increase in corrosion resistance is associated with high nitrogen content ($\sim 21\%$), 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



Figure 8. Examples of applications for modified materials.

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.

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