

Formation of diamond like carbon films on materials for medical application

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The aim of this experimental work is to identify how the surfaces of materials that are most often used in medical implants and prostheses, affect the properties of the deposited amorphous carbon films. The DLC films were formed on the stainless steel, aluminium, polyetheretherketone (PEEK) and polycaprolactone (PCL) surfaces by PECVD method using C₂H₂ gas plasma and their properties was compared with the films deposited on silicon. The differences of the films properties were determined by a null-ellipsometry and Raman spectroscopy. It was found that the thicknesses of the carbon coatings deposited on metallic substrates are larger than on the silicon when the deposition conditions were the same. When the films are formed at high bias voltage the refractive index of the DLC films deposited on stainless steel are lower compared to the coatings on silicon but the extinction coefficients are higher. Raman spectra shows that sp² bonds concentration is higher in this case. When the ion energy is lowest (bias voltage -400 V), Raman spectroscopy shows that D peak isn't observed on the Si-deposited carbon coating, while the typical carbon amorphous coating is formed on the Al substrate. The thickness of amorphous carbon coatings deposited on the polymers depends on the bias voltage, and the optical properties depend on the type of polymer. The coatings deposited on PCL have a much higher refractive index than on PEEK.

Key words: amorphous carbon films, steel, aluminum, polyetheretherketone, polycaprolactone, Raman spectroscopy.

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Introduction

One of the most widely used forms of carbon are the amorphous carbon films, the purpose of which is to improve another material, change it's surface properties, thus enabling its wider use in various fields. Due to the growing usage of the carbon coatings in electronics and other industries, the main problem still how to reduce the internal stresses and adhesion to the substrate. To reduce these problems, various metal layers, metal oxide layers, metal impurities have been used [1]. Recently, the possibilities of applying the carbon coatings in medicine have been explored, especially in the production of medical implants and prostheses. The medical implants usually need to withstand high mechanical loads, friction and aggressive biological fluid environments that can cause the implant to corrode, decay, and accelerate its wear. Therefore, the implant material must be chemically and biologically inert and mechanically stable. In addition, the materials required for the manufacture of

the implants must be biologically safe, non-carcinogenic, non-toxic to the human body, inhibiting the formation of organic biofilms and bacterial growth [2-6]. For these reasons, the implants are made from corrosion-resistant materials with high biocompatibility: metals (titanium, stainless steel), metal alloys (titanium-aluminum-vanadium, cobalt-chromium-molybdenum alloys), ceramics (usually aluminum, zirconium and titanium compounds) or polymeric materials [2,3]. Mechanical wear of the implant due to corrosion and friction over time causes the undesirable phenomenon of metallosis: metal ions, atoms and molecules, as well as small fragments of implant wear can penetrate into soft biological tissues and spread throughout the body. This can cause cytotoxicity, allergic or implant rejection reactions, painful inflammation or infection of the surrounding tissues, and can lead to the development of tumors and cancer cells. The risk of implant relaxation, fracture, disintegration, and premature wear also remains relevant [2,3,6-8]. As a result, the non-metallic polymeric implants have been increasingly

used in recent years. Nowadays, this kind of material are polyetheretherketone (PEEK) and polycaprolactone (PCL). In order to avoid adverse effects on the human body, they could completely replace traditional, flawed raw materials such as titanium or others in the future [9]. In many cases, the efficiency and biocompatibility of implants are determined by the surface properties, so the possibilities modifying the surface with biologically, mechanically, and chemically stable materials lets to obtain effective results [4-7, 10]. The amorphous carbon coatings are one such material, especially diamond like carbon (DLC) coatings, which have high hardness, low coefficient of friction, chemical inertness, good wear and corrosion resistance, biocompatibility, hemocompatibility and antibacterial properties. Various studies of the amorphous carbon coatings on implant materials have shown that such coatings have the ability to increase surface hardness, resistance to abrasion, corrosion, scratch, improve surface hydrophilicity, promote bone cell growth and adhesion, and weaken bacterial adhesion. Good carbon biocompatibility is associated with structure of organic compounds in the human body [2-4, 6, 8, 11]. DLC coats and films usually are deposited by plasma enhanced / activated chemical vapor deposition (PECVD). One of the main advantages of this method is that the deposition can be performed at low temperature (up to 200° C) without heating the sample, so no structural damage occurs in the material, less thermal stresses occur. Therefore, temperature-sensitive materials can be coated by this method. On the other hand, the reactive particles required for the growth of the coating are generated not by high temperature, but by plasma – glowing discharge, therefore DLC coating grown at low temperatures has good tribological properties [3,5,8,12,13]. The hydrocarbon gases are usually used as carbon and hydrogen sources in the deposition of films by this method: methane, acetylene, ethylene and benzene gases are the most common. [8,12,14,15].

Experimental setup

The DLC films were formed on the silicon, stainless steel, aluminium, polyetheretherketone (PEEK) and polycaprolactone (PCL) surfaces by PECVD method using C_2H_2 gas plasma. The temperature of the substrate was 25 °C, the pressure in chamber 10,7 Pa, the bias voltage variate from -400 V to -670 V, the power density 106 kW/m². Duration of the deposition was 60 s and 180 s, the bombarding ion energy

was 200 eV. The differences of the films properties were determined by a null-ellipsometry (Gaertner L117 with a He–Ne laser (632.8 nm)) and Raman spectroscopy (Ivon Jobin spectrometer with a Spectra Physics YAG:Nd laser (532.3 nm, 50 mW, spot size 0.32 mm)). The experimental RS curves were fitted by few Gaussian-shape lines in the spectral range from 600 cm⁻¹ to 1800 cm⁻¹,

Results

In order to understand how the metallic substrate influences the formation of carbon coatings compared to the semiconductor material, carbon coatings on the silicon and stainless steel were formed in the initial stage of the study. The main results are presented in Table 1. The deposition duration was 180s, power density 106 kW/m² bias voltage -650 V. The Raman spectra of the obtained films are presented in Fig. 1 a, b. The synthesis of Raman spectra showed that the positions of the typical amorphous carbon peaks D and G do not coincide, although the films were deposited during the same process. The Raman peaks (Fig. 1b) at 797 cm⁻¹, 1051 cm⁻¹, 1187 cm⁻¹ are related to the oscillations of the substrate (stainless steel) structure. Interestingly, that in the case of the film formation on the steel, the typical G band splits into two clearly separated peaks: at 1502 cm⁻¹ assigned to linear C=C bonds without hydrogen and 1588 cm⁻¹ related to the crystalline graphitic structure [16]. The G peak in the case of silicon is at 1518 cm⁻¹. The position of the D peak in the spectra of films formatted on the steel is strongly shifted towards the higher values (at 1391 cm⁻¹) and it correlates with the G band at 1588 cm⁻¹ [17]. It shows that the sp² bonds are predominated in this film. Meanwhile, the position of the G peak at 1518 cm⁻¹ and the position of the D peak at 1335 cm⁻¹ in the case of silicon indicate that this film has a large number of sp³ bonds [18]. In order to make sure that the metal substrate influences to the formation and structure of the coating, the films were formed on the aluminum substrate under the same process conditions. In the Raman spectra of films formed on the aluminum substrate (Fig. 1c), the positions of the G and D peaks were slightly shifted to the higher values in comparison with silicon case. The D2 peak at 1618 cm⁻¹ related with sp² bonds defect were obtained in the spectra [19]. The peaks in the spectra at 796 cm⁻¹, 1049 cm⁻¹, 1160 cm⁻¹, and 1209 cm⁻¹ belong to the aluminum substrate and were not analyzed here.

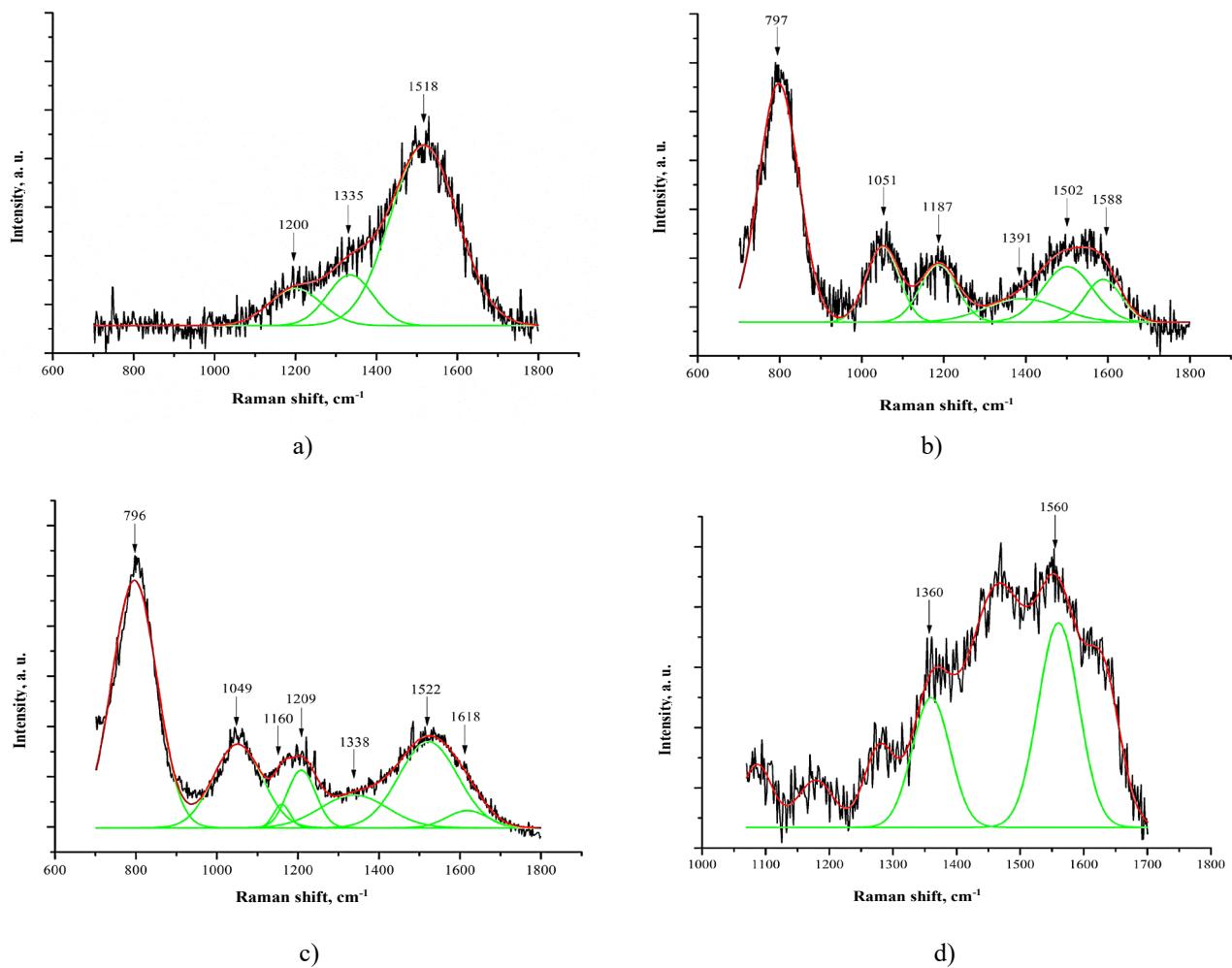


Figure 1 – Raman spectra of amorphous carbon films formed on silicon (a), stainless steel (b), aluminum (c) and polyetheretherketone (PEEK) (d). Condition of the formation: bias voltage -650V, power density 106 kW/m², duration 180 s.

Table 1 – The main characteristic of films formatted on silicon (*Si*), stainless steel (*steel*), aluminum (*Al*), polyetheretherketone (*PEEK*) and polycaprolactone (*PCL*). Deposition duration 180 s, bias voltage -650V, power density 106 kW/m²

Substrate	Thickness, nm	Refractive index	Extinction index	D peak position, cm ⁻¹	G peak position, cm ⁻¹	Ratio I_D/I_G
<i>Si</i>	779	1,88	0,04	1335	1518	0,19
<i>Steel</i>	783	1,80	0,13	1391	1588	0,82
<i>Al</i>	928	2,14	0,04	1338	1522	0,44
<i>PEEK</i>	498	1,5	-	1360	1560	0,63
<i>PCL</i>	536	2,16	0,02	1366	1546	1,03

The films were formed on PEEK and PCL for determining the influence of polymeric surfaces to the carbon films formation. Various types of carbon bonds and carbon bonds with hydrogen and oxygen predominate in the polymeric materials

themselves. In the Raman spectra of pure polymeric materials, among other carbon peaks, the D and the G bands characterized sp^2 and sp^3 compounds are observed also in the range of 600 cm⁻¹ to 1800 cm⁻¹. Therefore, the changes of the peaks position

of these bands and the changes of the I_D/I_G ratio have been analyzed after formation of the DLC films on these substrates. In the case of the pure PEEK, the peak of D band is at 1375 cm^{-1} and the G band – at 1552 cm^{-1} , the intensity ratio I_D/I_G of these peaks is 0.59. It was obtained that the peak of the D band was shifted toward the lower energies when the film was formed on the PEEK (Table 1 and Fig 1d). The peak of the G band also moved to the higher means, the ratio I_D/I_G ratio increased, and that changes indicated that the number of sp^3 bonds slightly increased also. The peak of the D band at 1365 cm^{-1} , the G band at 1548 cm^{-1} and

the I_D/I_G ratio about 0.93 were obtained in the Raman spectra of pure PCL. After deposition of the DLC film on the PCL the peaks positions did not change, but the ratio I_D/I_G also increased (Table 1). Thus, the higher quantity of sp_3 bonds is dominant in this film. The refractive index of pure PEEK is 1.67 [20], but the refractive index of the obtained coating is significantly lower than in the case of Si or metal substrate. Meanwhile, the refractive index of pure PCL was 1.46–1.49 [21], but the refractive index of the structure with the film is higher than films deposited on the PEEK, and is similar to that of the films on metal substrates.

Table 2 – The main characteristics of the DLC films deposited on different substrate with various bias voltage. Deposition duration 60 s.

Bias voltage	Substrate	Thickness, nm	Refractive index	Extinction index	D peak position, cm^{-1}	G peak position, cm^{-1}	Ratio I_D/I_G
-400V	Si	47	1,90	0,39	-	1512	-
	Al	85	2,08	0,02	1300	1547	0,35
	PEEK	73	1,88	0,34	1372	1551	0,67
	PCL	244	2,13	0,05	1360	1550	1,11
- 650V	Si	232	2,10	0,11	1331	1510	0,12
	Al	272	2,14	0,04	1338	1522	0,44
	PEEK	174	1,53	-	1370	1544	0,69
	PCL	218	2,32	0,06	1363	1547	1,46
-670V	Si	280	1,90	0,14	1371	1521	0,02
	Al	150	2,00	0,20	1290	1592	0,5
	PEEK	239	1,51	-	1374	1551	0,68
	PCL	249	2,25	0,04	1362	1548	1,85

For the obtaining the influence of the bias voltage to the properties of DLC films, formed on the various surfaces, deposition process were going in the three different regimes with bias voltage -400V, 650V and 670 V. The deposition duration was 60 s. The films formed on the silicon and aluminum surface were more sensitive to the changes of the bias voltage were (Table 2). In the case of the polymeric substrates, the position of the G peaks in the Raman spectra of the films deposited on the PCL and the PEEK are very similar, but the position of the D peak are variable. The I_D/I_G ratio in the case of the PEEK is almost independent on the ion energy, in the case of the PCL increased with increasing the bias voltage and the ion energy, while in the case of Si the opposite trend were seen.

Discussions

After the formation of the DLC films, it was found that the thicknesses of carbon films deposited on metal substrates (steel, Al) are larger than on Si when the deposition conditions are the same. When the coatings are formed at a bias voltage of -650 V (power density 106 kW / m²), the refractive index of films formed on the steel are lower compared to the films on the Si, but the extinction coefficients are higher. These changes are due to the amount of sp^2 bonds in the coating: the films are formed on the stainless steel with a higher concentration of sp^2 bonds and more ordered graphite net were obtained in this case (the shift of the G peak to higher value) than on the Si. The higher I_D/I_G ratios (0.62) of the films on the steel is conditioned of

existence lot of amount C=C bonds (peak at 1502 cm⁻¹), but this peak also can be assigned to D3 band which is related to the amount of sp³ carbon bond between sp² carbon rings [22]. Therefore, the disordered graphite with sp³ bonds are formed on the steel. It can be explained that the high-energy ions are bombarded the steel surface and heated it. The similar processes are going and on the Al surface where Raman spectra shows that the G band is splitted and the D band peak is at higher value (Fig.1c) Higher temperatures of the surface are one of the condition to form the graphite like films. In the silicon case because of existing active hydrogens atoms in plasma, etching of silicon surface and deposition processes occurs together. Chemosorbed on the surface hydrogen can bond with carbon radicals and form chain type sp³ bonds. This process is conditioned the typical position of the D bands. The G band shifting to lower values also shows that benzene rings are disordered and chain vibration is predominant.

More typical amorphous carbon films are forms on the metallic surface when the films are deposited with lower ion energy (bias voltage was -400V) during short process (60 s) (Table 2). The Raman spectra of the films on the Al shows the typical D and G bands at 1300 cm⁻¹ and 1551 cm⁻¹. Because of the thickness of layer is less, the net of sp₃ bonds is more ordered, so the D peak are at lower position. On the silicon surface are formed layer with high number of defects, including the bond length and angle disorder at the atomic scale, so there it is found only the peak G at 1518 cm⁻¹. This structure has the higher extinction coefficient and lower refractive index, than the Al case (the extinction coefficient 0.39 and 0.02; the refractive index 1.9 and 2.08, respectively). With increasing the bias voltage and ion energy during (-650 V and -670 V, power density 106 kW/m²) the deposition process, the films on the silicon and the Al become more typical as DLC films. In the case of silicon the ion energy dependence on the relative amount of sp² bonds is inverse (the I_D / I_G ratio decrease from 0.12 to 0.02), but in the case of the Al substrate, the ratio of sp² and sp³ bonds not change (I_D / I_G ratio 0.44). The refractive index of the films not depend on the substrate and ion energy, extinction coefficient were more sensitive (Table 2).

The refractive indexes of the DLC films on the PEEK are always lower, but on the PLC are higher in comparison with the films deposited on the silicon under the same process conditions. The ellipsometry measurements of these films showed that the thickness of films increases with increasing the bias voltage and ion energy. The thickness of the films deposited on PCL are significant higher in comparison with

other cases. The PCL is relative soften material in comparison with the silicon or the PEEK, so the ion bombardment during deposition easy can destroy deeper layers in the material. The boundary between the damaged layer of the material and the layers of formed film are disappeared. Calculation of the optical parameters of the pure films from ellipsometry measurements become complicated. For that reason, it was decided that in the case of PCL significant is full damaged and coated layer. The refractive index of amorphous carbon films deposited on polymers is practically independent on the bias voltage or the ion energy: it varies from 2.23 to 2.32, the extinction coefficient from 0.03 to 0.06 at the PLC case; the refractive index of the films on PEEK changed not significant (from 1.43 to 1.53). In others hands, the Raman spectroscopy showed that the relative number of sp² and sp³ bonds in the DLC films deposited on PLC depends on the ion energy – the I_D/I_G ratio increases with increasing the bias voltage. The relative number of sp³ and sp² bonds is independent on the bias voltage when the films are deposited on PEEK. Changes of the G peak shows that fragmentation of sp² bonds also changed, but in all cases the sp³ bonds still predominate in the coatings.

Conclusions

It was found that the thicknesses of carbon coatings deposited on the stainless steel and aluminum are larger than on silicon when the deposition conditions are the same. When the films are formed at bias voltage e of -650 V (power density 106 kW/m²), the refractive index of the DLC films deposited on the steel are lower in comparison with films coated on Si, and the extinction coefficients are higher. The films formed on stainless steel has higher concentration of sp² bonds than on Si (ID / IG ratios 0.62 and 0.19, respectively). The Raman measurements shows that the D peak is no observed in the spectra of the Si-deposited carbon films, so defected graphite net are formed there when the ion energy is the lowest (bias voltage -400 V) and deposition duration is about 60 s, but a typical amorphous carbon films are formed on the aluminum substrate. As the bias voltage increases (-650 V and -670 V), typical amorphous coatings form on both substrates (Si and Al). In this case, the substrate hardly changes the refractive index, but changes the extinction coefficient. The thickness of amorphous carbon coatings deposited on polymers depends on the bias voltage, and the optical properties depend on the type of polymer. Coatings deposited on the PCL have much higher the refractive index than on the PEEK.

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