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Deposition of carbon structures at atmospheric pressure by plasma jet

L. MARCINAUSKAS[a,b*], A. GRIGONIS[a], P. VALATKEVIČIUS[b]
[a]*Department of Physics, Kaunas University of Technology, Studentu 50, LT-51368 Kaunas, Lithuania,*
[b]*Lithuanian Energy Institute, Plasma Processing Laboratory, Breslaujos 3, LT-44403 Kaunas, Lithuania*

The carbon coatings were prepared on the steel substrates from Ar/C_2H_2 gas mixture at atmospheric pressure by plasma jet technique. The Ar/C_2H_2 gas volume ratio was 100, 150, and 200, while the distance between plasma torch nozzle exit and the samples was 0.005÷0.02 m. Scanning electron microscopy analysis demonstrated that the surface roughness and growth rate of the coatings increases with the Ar/C_2H_2 ratio. RBS and ERD results showed that the hydrogen and oxygen concentrations in the coatings decrease with the decrease of the deposition distance. Raman spectroscopy indicated that the film prepared at 0.005 m has the highest sp^3 C-C fraction, while the coating prepared at 0.02 m has the highest fraction of sp^3 CH_x bonds.

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1. Introduction

Recently much attention has been focused on the synthesis and investigation properties of various amorphous carbon coatings (amorphous hydrogen-free (a-C), hydrogenated (a-C:H)) and nanostructures (nanotubes, fullerenes, nanoonions) [1-3]. The unique properties (high hardness and wear resistance, low friction coefficient, chemical inertness, optical transparency, and etc.) of amorphous carbon are characterized by a combination of sp^2 and sp^3 sites fraction and the hydrogen concentration. The deposition method and process parameters allow to control and obtain carbon coatings with a desirable sp^2/sp^3 carbon sites fraction and hydrogen content. Thus deposit a carbon films with totally different properties and due to it adjusts these films in a various (optical, biomedical, electronic) application fields [1-3].

Nowadays a wide range of chemical and physical vapour deposition techniques are used to prepare carbon coatings [1, 4-8]. The main advantage of the plasma jet technique is a possibility to produce a different carbon phases such as diamond, a-C:H, nanoclusters, and etc. at reduced or even at atmospheric pressure. Also the coatings growth rate is usually about 10 to 100 times higher compared to the growth rates achieved by most PVD or CVD techniques [1, 8-14].

As was mention, the quality and properties of the coatings are strongly dependent on the process parameters. Many authors indicated that the power of the torch, anode nozzle construction, the substrate temperature, the deposition distance, the hydrocarbon gas type and its amount influence to the composition and densities of various species in plasma flow and as a consequence the structure and properties of carbon films will be different [8-15]. Pereira et al. [12] observed that the films produced at lower C_2H_2 gas flow rates are compose from the higher fraction of the sp^3 sites. Zaharia et al. [10] demonstrated that the growth rate was higher for films produced from an acetylene gas than methane. Benedikt et al. [13-14] indicated that the acetylene flow rate, discharge current, and distance changes the plasma composition and due to it properties of a-C:H coatings are changed. However, the studies concerning the formation of carbon structures in plasma under atmospheric pressure are still hard to find in the scientific-technical literature.

In this paper, the carbon coatings were obtained by plasma jet technique at the atmospheric pressure. The effect of the various Ar/C_2H_2 ratios and distances (plasma torch – substrate) on the growth rate, surface morphology, bonding structure, elemental composition, and optical properties of produced carbon films was investigated.

2. Experimental setup

A 5 kW power direct current (DC) plasma torch was used to deposit carbon films on the stainless steel substrates at the atmospheric pressure. The DC plasma torch consists of the copper cathode with the hafnium emitter, the feed gas injecting ring, and a step-formed anode nozzle containing the blowhole for the acetylene gas introduction [16]. The plasma jet is produced by arc discharge between the nozzle anode and cathode. Argon (flow rate of 6.6 l/min) was used as plasma forming gas, and acetylene as a precursor. The acetylene gas flow was varied in the range of 0.033-0.066 l/min. The substrates were polished, chemically cleaned with acetone and kept for 30 s in argon plasma before starting the deposition. The plasma torch power was ~600 W and the deposition time - 120 s. The detailed formation conditions and thickness of the deposited carbon films are shown in Table 1.

Table 1. The preparation parameters of the carbon films.

Ar/ C_2H_2 volume gas ratio	Distance [m]	Plasma temperature [°C]	Thickness of the films [µm]
150	0.005	950	~0.450
150	0.01	585	~1.5
150	0.015	385	~3.5
150	0.02	275	~2.0
100	0.02	260	~5.0
200	0.02	260	~1.0

The surface morphology and thickness were investigated by scanning electron microscope (SEM) model JEOL JSM-5600. The plasma flow temperature above the substrate was measured by chromel-aliumel (X-A) thermocouple. The temperature measurements were performed several times due to calculate an average plasma flow temperature. The bonding structure and optical properties of carbon structures were characterized using Raman scattering (RS) and Fourier transform infrared (FTIR) spectroscopy. The FTIR reflectance spectra were obtained using a Perkin Elmer spectrometer (model Spectrum GX FTIR). Raman spectra were collected by a conventional grating Raman spectrometer, by using an argon ion laser (514.5 nm) as the source for excitation. The depth distributions of elements were measured by Rutherford backscattering spectrometry (RBS) using a 1.5 MeV proton beam at a scattering angle of 170°. Hydrogen concentration was obtained by elastic recoil detection (ERD), which was performed using helium ($^4He^{+2}$) ion beam with 1.5 MeV energy and with 80° beam-incidence angle to the surface normal.

3. Results

The temperature measurements demonstrated that the plasma temperature above the formed samples increases with the decrease of distance (Table 1). However, the variation of the acetylene flow almost has no influence on plasma temperature. Despite it, the alternation of the Ar/C_2H_2 ratio will cause changes of hydrocarbon species densities in plasma, as a result of this; the surface morphology, and bonding structure of the coatings mutates.

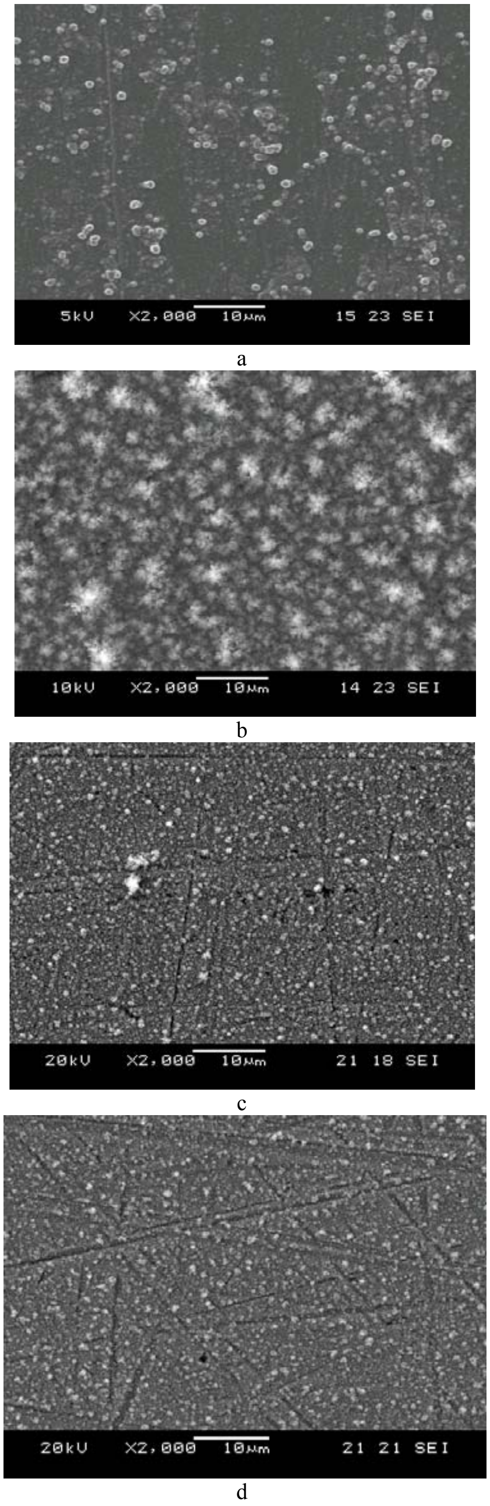

Fig.1. SEM micrographs of films deposited at (a) Ar/C_2H_2=150 and 0.005 m, (b) Ar/C_2H_2=100 and 0.02 m, (c) Ar/C_2H_2 = 150 and 0.02 m, (d) Ar/C_2H_2=200 and 0.02 m.

With the decrease of the Ar/C_2H_2 ratio, as illustrated in Fig. 1, the surface roughness of the coatings increases. The film prepared at Ar/C_2H_2=100 is porous and consist from ~5 µm size snowflake-like fragments. As the acetylene flow decreases the surface is covered by 0,5-1 µm size agglomerated grains. The film deposited at 0.005 m distance is smooth and covered by randomly situated 0.5-1 µm size grains (Fig. 1a). As the deposition distance increases the surface of the coatings become rougher and consisted from the micrometer size irregular fragments (Fig. 1c).

As can be seen from Fig. 2, the absorption bands of films prepared at 0.02 m distance are similar. However the character of spectrum of the coating deposited at Ar/C_2H_2=100 is different from the others. It can be observed that the increase of the Ar/C_2H_2 ratio leads to the widening of the OH (~3400 cm^{-1}) and C=O (~1725 cm^{-1}) bonds [6]. It indicates that the oxygen concentration in the films become higher. Three peaks were found in the region 2800–3000 cm^{-1}. The band at ~2960 cm^{-1} represents sp^3 CH_3 anti-symmetric vibration and the other two vibrations at around 2930 and 2860 cm^{-1} are assigned to sp^3 CH_2 asymmetric and symmetric stretching modes, respectively. Presence of sp^3 CH_3 bonding in the coatings is further confirmed by the sharp absorption band at 1390 cm^{-1} [1]. The intensity of these bands becomes deeper with the decrease of the acetylene flow. The broad peak at 1600 cm^{-1} is attributed to the presence of the sp^2 C=C bonds. The broad peak centered at 1120 cm^{-1} is related to C-O-C stretching vibrations [5, 11].

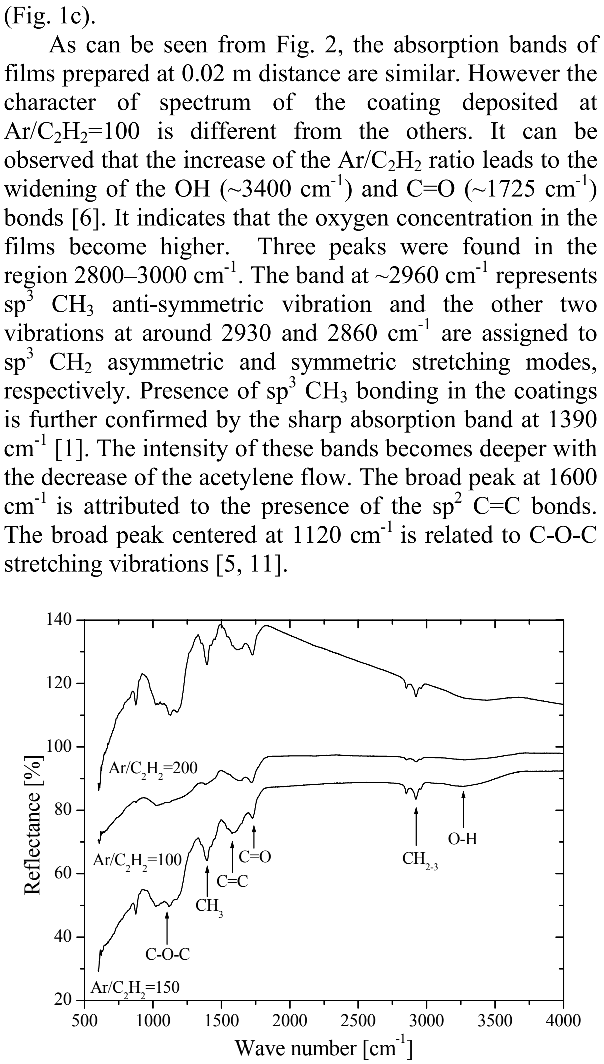

Fig.2. FTIR spectra of carbon coatings deposited at 0.02 m.

The nature of FTIR spectra of the films prepared at Ar/C_2H_2=150 and various distances are very similar. The wide band at 1580 cm^{-1} is assigned to the vibrations of sp^2 C=C bonds and indicates that the carbon bonds are in aromatic and olefin configurations [5, 6]. The shift of the peak position to a higher wave number range (from 1570 to 1585 cm^{-1}) with the increase of the deposition distance is related to the increase of the olefin carbon structures in the films [6]. The band with the absorption maximum at 1725 cm^{-1} in FTIR spectra of the carbon films is attributed to the C=O stretching vibrations. Besides, a broad peak also appears at 3400-3500 cm^{-1} due to O–H stretching mode. This shows that the deposited structures are oxy-hydrogenated as well [6]. Also the bands related to sp^3 CH_{3-2} (~2960, 2930, and 2860 cm^{-1}) asymmetric vibration and symmetric stretching modes are present in the spectra.

The RBS and ERD results indicated that the hydrogen and oxygen concentration increases with the increase of distance. The film deposited at 0.005 m mainly consist of carbon (94 at.%) with a low concentration of the hydrogen (~3 at.%) and oxygen (~3 at.%). While the coating deposited at 0.02 m have up to 32.5 and 18 at.% of hydrogen and oxygen, respectively. Meanwhile, for the films deposited at 0.02 m, the highest hydrogen concentration was when Ar/C_2H_2 ratio is 150. The coating deposited at Ar/C_2H_2=200 has about 27 at.% of hydrogen.

Raman spectroscopy was used to characterize the bonding structure of the carbon films. The uprising spectra of the coatings deposited at 0.02 m (Fig. 3) are related with a polymeric nature [1]. The coating obtained at Ar/C_2H_2=100 consist from two separate high intensity G (1605 cm^{-1}) and D (1397 cm^{-1}) bands. The full width at half-maxima (FWHM) of the D and G peaks is 203 and 78 cm^{-1}, respectively. The intensity ratio between the D and G peaks (I_D/I_G) of the film is 1.83. The high I_D/I_G ratio, narrow G peak, and shape of spectrum indicate that beside the polymeric CH_x sites, the coating has high fraction of sp^2-bonden carbon [7]. The increase of the Ar/C_2H_2 influences broadening of the FWHM for D (250 cm^{-1}) and G (160 cm^{-1}) peak. The RS results indicated that the coating deposited at Ar/C_2H_2=150 is typical polymer-like carbon. The film deposited at Ar/C_2H_2=200 has D peak lied at 1388 cm^{-1} (with FWHM of 187 cm^{-1}) and G at 1606 cm^{-1} (with FWHM of 97 cm^{-1}). While the I_D/I_G ratio is 1.34.

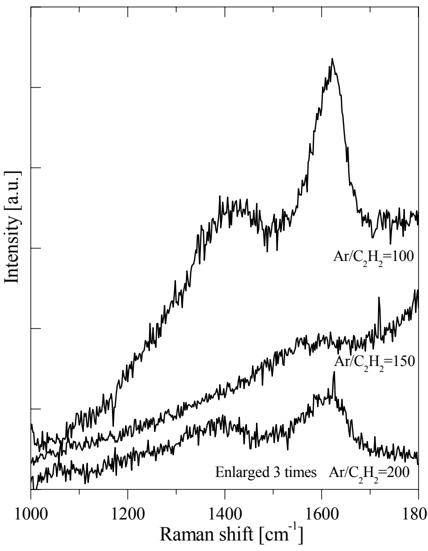

Fig. 3. RS spectra of carbon structures deposited at various Ar/C_2H_2 at 0.02 m. The intensity of the RS spectrum of the film prepared at Ar/C_2H_2 = 200 was enlarged 3 times.

As can be seen the film formed at 0.005 m has two separate and almost the same intensity D centered at 1350 cm^{-1} (with FWHM of 164 cm^{-1}) and G at 1607 cm^{-1} (with FWHM of 92 cm^{-1}) bands (Fig.4). The I_D/I_G ratio of the film is 1.26. This result indicates that a diamond-like carbon coating with the glassy carbon phase inserts was deposited [7, 17]. It was obtained that the position of the G peak shifts from 1607 to 1615 cm^{-1}, the FWHM of the G become broader (changes from 92 to 186 cm^{-1}), while the FWHM of the D peak get narrower (from 164 to 120 cm^{-1}) with the increase of the distance from 0.005 m up to 0.015. The I_D/I_G ratio slightly increases from 1.26 reaches the highest value (1.41) at 0.015 m, and when decreases down to 0.31 (at 0.02 m). Generally, increasing of the I_D/I_G and shifting of the G-peak toward higher wave number are caused by the increase of the graphite-like component in the a-C:H films and the sp^2-bonded carbon clusters size [17]. However, the broadening of the G peak usually indicates higher bond length and bond angle disorder and higher fraction of sp^3 C-C [1].

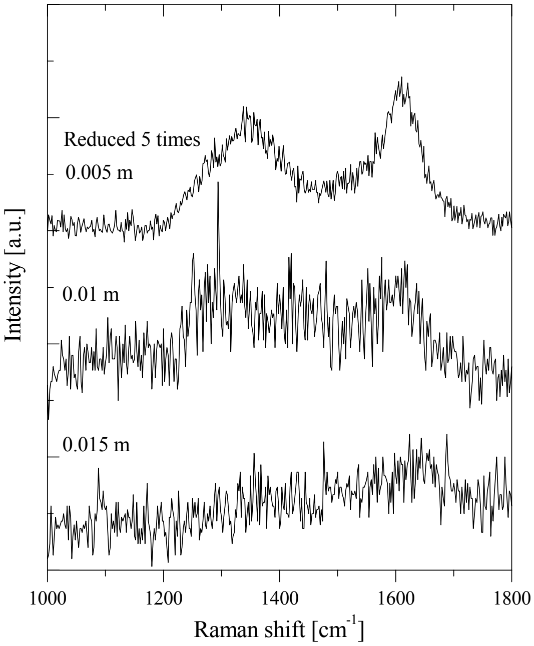

Fig. 4. RS spectra of carbon structures deposited at various distances. The intensity of the RS spectrum of the film deposited at 0.005 m was reduced 5 times.

The variation of the distance also results in a different shape of RS spectra. The RS spectrum of the films prepared at 0.01 m beside D and G peaks has bands at 1120 and 1440 cm^{-1}. The appearances of these bands suggest the presence of nanocrystalline diamond phase and the existence of disordered sp^3-bonded carbon [18]. The changes obtained in the RS spectra lead to suggestions that the hydrogen concentration in the films increases with the distance [1, 18]. The decrease of I_D/I_G ratio at 0.02 m is explained by the increase of sp^3 CH$_3$ polymeric chains regarding the decline of sp^2 carbon sites in the coating [10].

4. Discussion

The performed investigations indicated that the variation of the Ar/C$_2$H$_2$ ratio and distance affects the surface morphology and bonding structure of the films. The substitution of these parameters will change the processes and chemical reactions in the plasma; as a consequence the composition of deposited films would be transformed. Benedikt et al. [13-14] demonstrated that with the decreasing the acetylene flow rate more C_2H_2 is fully decomposed into H, C, C_2, and CH species. As a result the growth rate decreases, but obtained coatings will have higher fraction of the sp^3 sites. So it is believed that the increase of the Ar/C_2H_2 ratio from 100 to 200 will lead to a full decomposition of acetylene and changes the nature of reactive species arriving to the surface. Thus, the flux density of the atomic hydrogen and carbon will be the highest. The ERD results indicated that the highest content of the hydrogen is obtained in film prepared at Ar/C_2H_2=150. RS results also demonstrated a typical polymer-like carbon spectrum. Thus these conditions allow the production of coatings with the highest fraction of polymeric CH$_x$ sites. The film deposited at Ar/C_2H_2=200 has a lower content of the hydrogen (27 at.%), which is typical for a diamond-like carbon films [1]. However a high fraction of the oxygen (16 %) blocks the formation of the sp^3 C-C. FTIR spectrum demonstrated an absorption bands related to carboxyl and OH groups. Presence of these bands in the a-C:H films according to Louh [6] shows a large concentration of free radicals. Thus due to interaction of the plasma jet with the ambient air, the oxygen will bond with the dangling sites, and creates C=O, C-O or O-H sites.

The shape of RS spectra indicated that with the increase of the distance the coatings have higher fraction of the polymeric sites, due to the increase of the hydrogen concentration. Neyts et al. [15] obtained that the H content in the film increases with the increase of the H flux towards the substrate. The low concentration of the hydrogen in the film prepared at 0.005 m, is explained by the high formation temperature and reactivity of the atomic hydrogen. H will easily bond and creates H_2 also at high temperatures it will easily desorb from the coating. Zaharia et al. [10] demonstrated that the films obtained at the higher temperatures are harder due to the formation of more sp^3 C-C bonds. It is well known that the hydrogen etches the graphitic phase and creates dangling sites [1]. Thus the increase of the H flux stipulates a conversation of the sp^2 C=C into sp^3 C-C. However, probably due to high density of H in the plasma flow the C-C sites are broken and immediately replaced by C-H. So the coatings will have high fraction of polymeric sites. The RS results confirmed these facts. However the sp^2/sp^3 ratio increases despite the increase of the hydrogen when the distance changes from 0.005 to 0.015 m. It may be noted that the increase of the distance will result to different chemical reactions; the light radicals will react each to other creating a heaver species (C_2H, C_3H, C_2H_4) [13-14]. Generally, the films containing >20 at.% of hydrogen are diamond-like carbon [1]. However, during the formation of the coatings by plasma jet, the hydrogen creates the sp^3 C-H sites (polymeric phase) or C_2H radicals which are in sp^1 bonding. Also due to interaction of the plasma jet with the ambient air, the oxygen will bond with the different radicals. So with the increase of the distance more oxygen will bond with the dangling bond of the carbon or hydrogen and the oxygen concentration in the coatings would be higher. It will results to the formation of the sp^2 C=O sites, as a result the fraction of the sp^3 C-C decreases. The RBS results demonstrated that the oxygen concentrations increased up to 6 times. These results indicate that the chemical reactions and process in the plasma are very complicated and still not well explained.

5. Conclusions

The carbon films have been formed at the atmospheric pressure using acetylene gas at various distances and Ar/C_2H_2 ratios. The coating formed at the shortest distance (0.005 m) has the highest fraction of sp^3 bonded carbon sites. The surface roughness and growth rate of the coatings increases with the decrease of Ar/C_2H_2 ratio. The concentrations of the hydrogen and oxygen increases with the increase of the distance (plasma torch – substrate) and as result the polymer-like carbon film is formed. The deposition distance and Ar/C_2H_2 ratio affects the growth rate, surface morphology, bonding structure, and elemental composition of carbon films.

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[*] Corresponding author: liutauras@mail.lei.lt,
liutauras.marcinauskas@ktu.lt