

INFLUENCE OF TORCH POWER AND Ar/C₂H₂ RATIO ON STRUCTURE OF AMORPHOUS CARBON FILMS *

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The amorphous hydrogenated carbon films (a-C:H) were formed on the stainless steel substrates from an argon–acetylene gas mixture at atmospheric pressure using a direct current plasma torch discharge. The carbon films were deposited using Ar/C₂H₂ gas volume ratios 100:1, 150:1, and 200:1 and plasma torch power of 600 and 870 W. It has been obtained that the increase of the torch power leads to higher film growth rate and increases surface roughness. The growth rate varies from 20 up to 425 nm/s depending on the coating formation conditions. The structure and dominant bonds of the films were investigated by Fourier transform infrared (FTIR) and Raman spectroscopy (RS) measurements. RS results indicated that the sp²/sp³ content in the films depended on the torch power and C₂H₂ amount in argon plasma. It was demonstrated that a diamond-like / graphite-like carbon and glassy carbon films could be deposited by varying the Ar/C₂H₂ ratio and plasma torch power.

Keywords: plasma torch, carbon films, acetylene, structure

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1. Introduction

Nowadays thermal plasmas are widely used for the production of ultrafine particles, formation of various coatings (ceramic, metal oxide, carbon), surface modification, or waste treatment [1–4]. The main advantage of this technique is the generation of high concentration of the reactive species (radicals, atoms) that can form a coating with high deposition rates due to steep gradients in the boundary layer plasma – substrate. It has been obtained that the growth rate of hydrogenated amorphous carbon films (a-C:H) or polycrystalline diamonds produced by arc plasma jet technique can reach up to 100 nm/s [4–7]. Meanwhile, the growth rates of a-C:H obtained by traditional chemical vapour deposition (CVD) or physical vapour deposition (PVD) techniques are ten or hundred times lower compared to the arc plasma jet [8–12]. The second advantage of this technique is the formation of carbon films at the atmospheric pressure conditions. However, despite these advantages, the deposition of a-C:H coatings is a complicated process and depends on many different factors [4–7].

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Many authors [4–12] have demonstrated that the hydrogen concentration and corresponding proportion of the sp² and sp³ carbon sites in the films determines the properties of carbon coatings. Variation of the deposition process parameters allows one to control and produce a-C:H films with desirable properties. It has been demonstrated that the type of hydrocarbon gases and its amount in plasma, the power of the torch, the pressure, the substrate temperature, and the plasma torch construction are very important factors during the deposition of films by plasma jet CVD [4–7].

There are many research works investigating the influence of these factors during the deposition of carbon films from methane gas by plasma jet. Meanwhile, the quantity of works that investigates the coating formation processes from the acetylene gas is significantly lower. The acetylene gas is also interesting for the possibility to obtain higher growth rates due to large carbon/hydrogen ratio. However, it poses a new challenge: to find optimal process conditions for the deposition of carbon films with desirable mechanical, optical properties. Zaharia et al. [5] have determined that the deposition rates in the acetylene gas is seven times greater than in methane. Benedikt et al. [6, 7] investigated the influence of the argon–acetylene gas ratios on

the a-C:H films growth kinetics and properties. Kessels et al. [13] focused on influence of the substrate temperature on the hydrogen content and the growth rate of a-C:H. However, these researches were done under the reduced pressure conditions. The production of a-C:H films at the atmospheric pressures by the torch flame method was done by Pereira et al. [14]. However, the films were grown from O₂–C₂H₂ gases mixture. Our previous works [15, 16] show that the acetylene gas content in Ar plasma may drastically change the surface morphology, structure, and optical properties of carbon films. The lack of information in the studies concerning the deposition of carbon films from Ar–C₂H₂ gases under the atmospheric pressure stipulates further investigation in this research area.

This paper introduces experimental analysis of carbon films prepared by plasma jet CVD at the atmospheric pressure. The aim of the work was to investigate the influence of the argon/acetylene ratios and input power on the surface morphology, growth rate, and bonding structure of deposited amorphous hydrogenated carbon coatings.

2. Experimental set-up

A 5 kW power direct current (DC) plasma torch was used to deposit carbon films onto 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 precursor gas introduction [15]. 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 feed gas, and acetylene (C₂H₂) as a precursor (0.066–0.033 l/min). The C₂H₂ gas is injected into the plasma flow of a high temperature region. The plasma torch powers were 600 and 870 W. The substrates were polished and chemically cleaned with acetone and kept for 30 s in argon plasma before the deposition. The duration of deposition was 120 s for all experiments. The distance between the plasma torch nozzle exit and substrate was 0.01 m. The detailed formation conditions of the carbon coatings are given in Table 1.

Scanning electron microscope (SEM), model JEOL JSM–5600, was used to characterize the surface morphology and through cross-sectional views the film growth rates were calculated. The plasma flow temperature above the substrate was measured by chromel-alumel (X-A) thermocouple. The bonding structure and optical properties of carbon films were measured

using Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra were obtained using a Perkin Elmer spectrometer (model Spectrum GX FT-IR). FTIR reflectance spectra were detected in the range of 670–4000 cm⁻¹ at spectral resolution of 0.3 cm⁻¹ using air as reference. Raman scattering (RS) spectroscopy was used for the structure characterization. The wavelength of the argon laser was 488 nm, and the spectra were recorded in the 1000–1800 cm⁻¹ range. In order to estimate the sp³/sp² ratio the RS curves were fitted by Gaussian-shape line.

3. Results and discussion

3.1. Surface morphology studies

The temperature measurements indicate that the plasma temperature above the deposited samples increases with the increase of torch power and C₂H₂ flow rate (Table 1). Plasma temperature rises from 600 up to 690 °C with changing torch power from 600 to 870 W, for films deposited at Ar/C₂H₂ = 100. This phenomenon is related to higher degree of dissociation of the acetylene gas at higher torch power.

The film prepared at 600 W and Ar/C₂H₂ = 100 consists of 200–500 nm size grains (Fig. 1(a)). As the Ar/C₂H₂ ratio increases, the surface of the coating becomes smooth and covered by randomly situated grains (Fig. 1(c)). Further increase of the argon–acetylene ratio leads to a lower concentration of the grains on the top of the surface (Fig. 1(e)). Meanwhile the grains interlink into ~10 μm size clusters at higher power and the existence of columnar structure of the coatings indicates the island growth (Fig. 1(b)). The well-ordered columnar structure disappears with decreasing the acetylene flow. The deposited carbon film indicates self-developed micro formations and contains many loosely adhered particles. The rough cluster formations, randomly distributed with deep holes between the clusters were obtained after deposition at Ar/C₂H₂ = 200 ratio (Fig. 1(f)).

The highest growth rate (425 nm/s) was obtained for the film prepared at Ar/C₂H₂ = 100 and 870 W. The increase of the torch power from 600 up to 870 W increases the growth rates up to 10 times. However, it was demonstrated that the faster deposition rate determines the increase of the surface porosity and roughness of the coatings (see Fig. 1).

The dependence of the growth rate on the input power could be expected due to high levels of torch

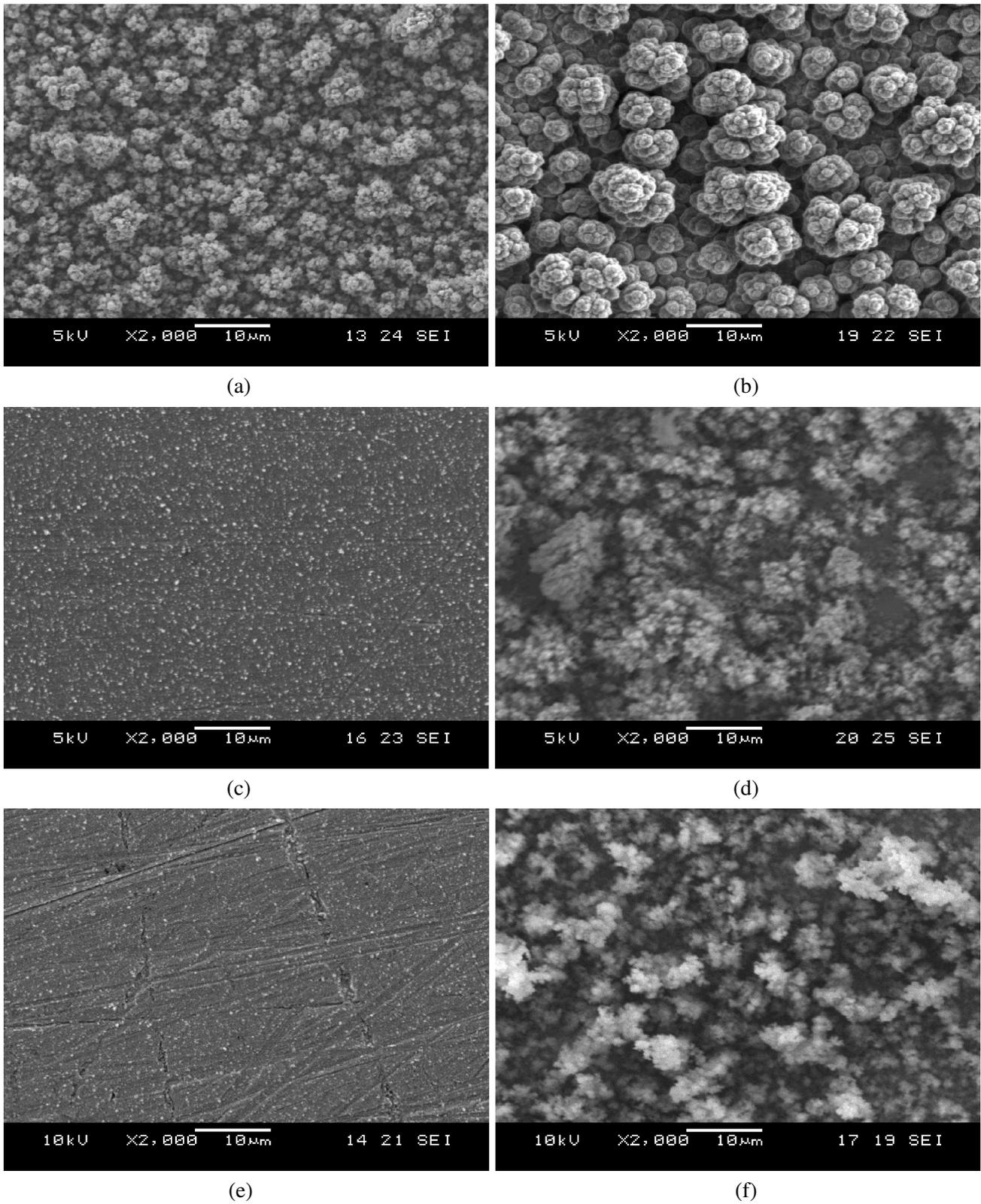


Fig. 1. SEM micrographs of films prepared at (a, c, e) 600 W and (b, d, f) 870 W plasma torch powers and different Ar/C₂H₂ ratios: (a, b) Ar/C₂H₂ = 100, (c, d) Ar/C₂H₂ = 150, (e, f) Ar/C₂H₂ = 200.

Table 1. Preparation conditions and growth rates of the carbon films.

Ar/C ₂ H ₂ volume gas ratio	Power [W]	Plasma temperature above substrate [°C]	Growth rate [nm/s]	Thickness of the films [μm]
100	600	600	35	4.2
150	600	585	25	3.0
200	600	570	20	2.4
100	870	690	425	51
150	870	660	300	36
200	870	640	125	15

power resulting in high levels of gas activation and dissociation, with the outcome of high densities of the hydrocarbon radicals in the plasma. The variation of the Ar/C₂H₂ ratio and input power will yield different plasma flow temperatures and surface processes. These results indicate that the plasma jet temperature and composition of the dominant species in plasma can be changed by varying the acetylene gas flow and especially torch power. Benedikt et al. [6, 7] determined that at high acetylene flows dominant radicals in plasma are C₂H, C₃H₂, C₄H₂, etc. With decreasing the C₂H₂ flow, more acetylene is fully decomposed into the atomic hydrogen, carbon, or light species (C₂, CH). As a result, the growth rate will decline, but produced a-C:H films will have higher fraction of sp³ sites. Meanwhile the rough and columnar structure surfaces will be formed when the heavy radicals will dominate in plasma flow (Fig. 1(b, d, f)).

3.2. Infrared spectroscopy results

The FTIR spectroscopy has shown that the highest reflectance values are at 4000 cm⁻¹, and slowly diminish with decrease of the wave number (Fig. 2). It may be noted that the reflectance values of the films obtained

at 600 W are higher than of those deposited at 870 W. This phenomenon could be explained by the morphology of the deposited surfaces. A strong broad band at 3400 cm⁻¹ corresponds to valence and deformation vibrations of O–H group. The intensity of the OH band increases with the decrease of the acetylene amount in argon plasma. This indicates higher dissociation degree of the C₂H₂ that causes higher concentration of the light radicals in plasma. These radicals will have dangling bonds which easily bond with arriving oxygen or OH. A band at 1720 cm⁻¹ is assigned to the stretching vibrations of C=O bonds in carboxyl and carbonyl groups. The band at 1590–1600 cm⁻¹ is assigned to the vibrations of C=C bonds. The broad band at around 1120 cm⁻¹ is related to C–O–C stretching vibrations [10, 11]. The spectra of a-C:H films shows presence of sp³ –CH₂ symmetric (2850 cm⁻¹) and asymmetric (2920 cm⁻¹) stretching modes, and existence of sp³ –CH₃ asymmetric (2955 cm⁻¹) group. Meanwhile, the peak at ~1390 cm⁻¹ is attributed to sp³ (CH₃)₃ bonded sites. The presence of the C–H_{2–3} stretching bands in the IR spectra indicates the films to be hydrogenated in their nature [8].

The absorbance band associated with OH group becomes wider and more intense with decrease of the

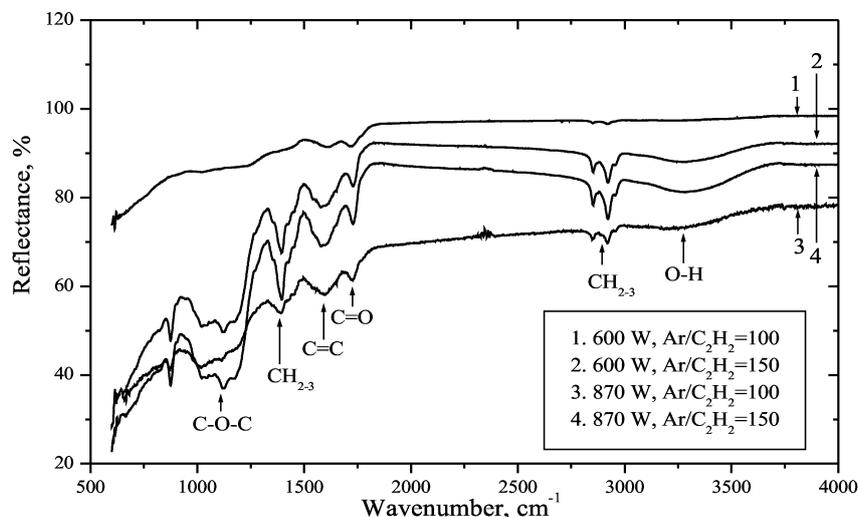


Fig. 2. FTIR spectra of carbon films deposited at Ar/C₂H₂ = 100 and Ar/C₂H₂ = 150.

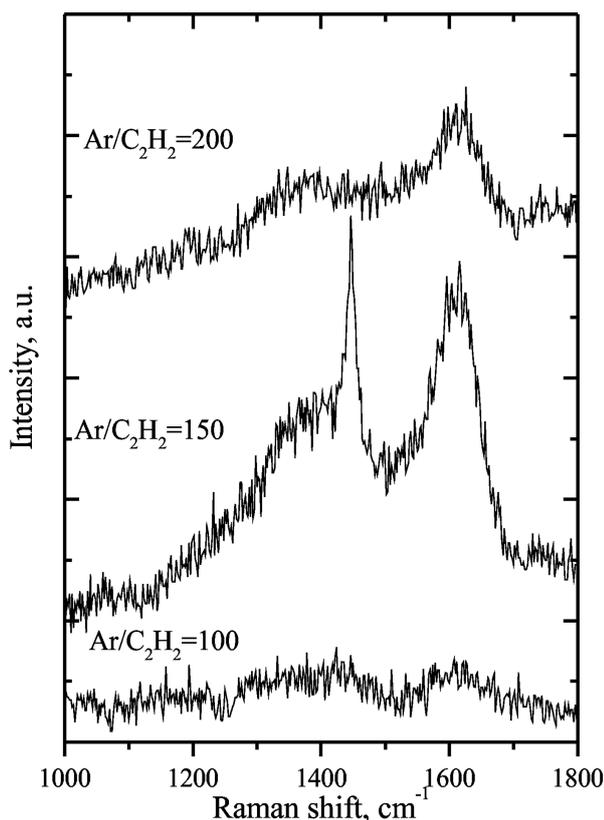


Fig. 3. RS spectra of carbon coatings deposited at 870 W torch power.

C_2H_2 flow. The presence of the carboxyl group becomes more intense and narrower, while sp^2 C=C absorbance band becomes deeper with increase of the torch power and Ar/ C_2H_2 ratio. It was found that increase of the Ar/ C_2H_2 ratio of the films deposited at 870 W induces the shift of C=C band to lower frequencies. This result indicates the increase of the aromatic carbon structures in the films [10, 11]. It has been observed that the relative intensity of sp^3 CH_{2-3} modes in the films increases with increasing torch power and decreasing acetylene flow.

3.3. Raman scattering spectroscopy

RS results indicate that the films have typical asymmetrical bands related to diamond-like carbon coatings [8]. The intensity ratio between the D and G peaks (I_D/I_G) of the films deposited at 870 W for Ar/ C_2H_2 = 100, Ar/ C_2H_2 = 150, and Ar/ C_2H_2 = 200 ratios are almost the same: 2.54, 2.53, and 2.46, respectively. This demonstrates a high fraction of the sp^2 phase in films. However, the shapes of these spectra are different (Fig. 3). For the film obtained at Ar/ C_2H_2 = 100 it consists of three low intensity wide bands: D (1386 cm^{-1}), G (1616 cm^{-1}), and a peak at 1150 cm^{-1} ,

indicating the existence of C–H vibrations in trans-polyacetylene-like chains. Meanwhile, the coating produced at Ar/ C_2H_2 = 150, beside D (1386 cm^{-1}) and G (1610 cm^{-1}) peaks, has a narrow band at 1447 cm^{-1} . This peak is attributed to a $C5 A_{g(2)}$ pentagonal pinch mode or due to relaxation of the photon selection rules for nanocrystalline materials [17, 18]. The film deposited at the highest Ar/ C_2H_2 ratio has only D and G peaks centred at 1382 and 1609 cm^{-1} , respectively. The increase of the Ar/ C_2H_2 ratio influences the broadening of the full width at half-maxima (FWHM) for D peak: from 210 to 269 and to 285 cm^{-1} . The broadening of the D band is related to the presence of large sp^2 carbon bond angle distortion [8]. The same tendency was obtained for the FWHM of the G band (increases from 74 to 86 cm^{-1}). Paul et al. [17] have proposed that the FWHM of the G peak would be small if the clusters were defect free, unstrained, or molecular. Thus, the broader FWHM would mean higher bond length and bond angle disorder and hence higher fraction of the sp^3 sites. The I_D/I_G ratios of the films indicate high fraction of the sp^2 bonded carbon. However the decrease of the I_D/I_G ratio with the increase of Ar/ C_2H_2 is associated with the increase of the sp^3 sites' fraction [8]. Separation of the D and G bands in the RS spectra (especially for Ar/ C_2H_2 = 150) indicate insufficient concentration of hydrogen and formation of a glassy carbon phase [9].

The coating deposited at 600 W torch power and Ar/ C_2H_2 = 100 has two separate peaks of the same intensity: D, 1382 cm^{-1} with FWHM of 195 cm^{-1} , and G, 1611 cm^{-1} with FWHM of 94 cm^{-1} (Fig. 4). The I_D/I_G ratio increases from 1.82 to 2.41 with increase of the argon–acetylene ratio from 100 to 200. Thus, the D (1410 cm^{-1}) and G (1617 cm^{-1}) bands are shifted to higher wave number range, compared to the typical D and G peaks [8, 17]. This is related to high internal stresses in the coating. The Raman studies also indicate that FWHM of the G peak becomes narrower (changes from 94 down to 74 cm^{-1}) compared with the films obtained at lower Ar/ C_2H_2 ratios. Thus, it demonstrates the formation of the graphite phase with small nanocrystalline grain size in coating [8]. According to these results the film produced at Ar/ C_2H_2 = 200 has the highest fraction of the sp^2 carbon sites.

It may be noted that the I_D/I_G ratio becomes lower with the decrease of the torch power from 870 to 600 W that indicates the higher fraction of the sp^3 sites in the films. The substrate and coating would be heated more with the increase of the plasma flow temperature and that would lead to the graphitization processes [9]. This

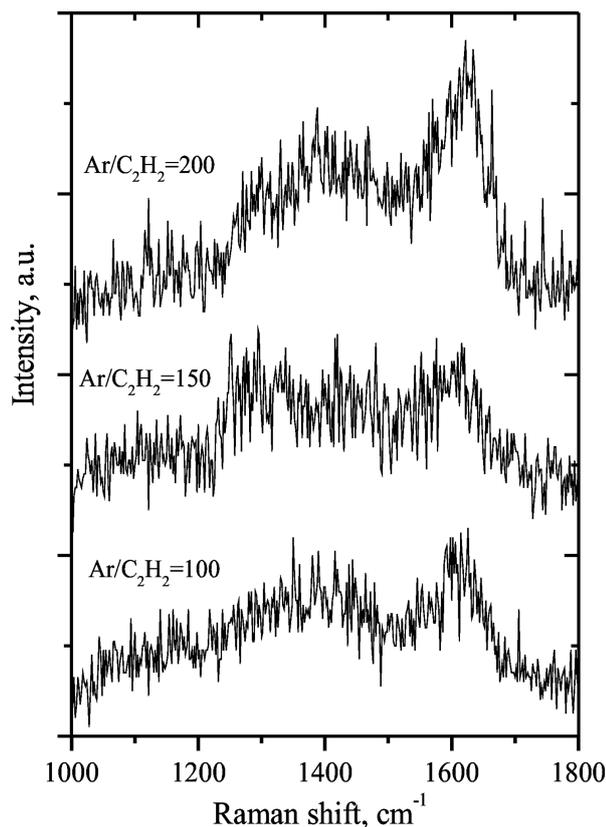


Fig. 4. Raman spectra obtained for carbon films deposited at 600 W.

suggestion was confirmed by the existence of a relatively higher fraction of sp^3 sites in films obtained at higher argon–acetylene ratios for 870 W powers. Also lower acetylene gas amount in plasma will result in higher flux densities of the atomic carbon and hydrogen or other light hydrocarbon radicals. These radicals will have dangling bonds which easily bond with arriving hydrocarbon species or oxygen. Because of that the fraction of the CH, C–C, C–O sites will increase with Ar/C₂H₂ ratio. Benedikt [6, 7] has obtained that the increase of the C₂H₂ flow stipulates the increase of the sp^2 bonded carbon content. However, the concentration of the oxygen goes down. RS results confirm that sp^2 bond fraction decreases with the increase of Ar/C₂H₂ ratio only for the films deposited at 870 W. Meanwhile, the opposite tendency was determined for the coatings produced at 600 W torch powers. FTIR spectra indicated that the intensity of absorbance bands related to the oxygen bonds with the carbon and hydrogen increased with increasing Ar/C₂H₂ ratio for the both torch powers. However, it is problematic to conclude on the influence of the torch power and Ar/C₂H₂ ratio on the type of dominant bonds in the films from the RS and FTIR spectra. The dissociation process also affects the surface morphology and growth kinetics of the

films. The columnar structure and porosity will influence appearance of the dangling sites. However, the atmospheric oxygen will easily bond with these dangling sites and will result in the growth of distorted a-C:H coatings. The optimal temperature for the DLC film formation has been 585–600 °C.

4. Summary

The acetylene dissociation rate, plasma flow temperature, and films' growth rate increases with the increase of the plasma torch power. However, the deposited coatings consist of the columnar structure and have a lot of oxygen sites bonded with carbon or hydrogen. Thus, the nature of the a-C:H is distorted. The a-C:H diamond-like films with more uniform surface morphology are deposited at 600 W torch power and it has been obtained that the fraction of the sp^3 phase depends on the Ar/C₂H₂ ratio.

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IŠLYDŽIO GALIOS IR Ar/C₂H₂ DUJŲ SANTYKIO ĮTAKA AMORFINIŲ ANGLIES DANGŲ STRUKTŪRAI

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Santrauka

Nagrinėjama amorfnių hidrogenizuotų anglies dangų (a-C:H) sintezė ant plieno padėklų, panaudojant atmosferos slėgio elektrolankinių nusodinimą iš argono–acetileno dujų mišinio plazmos. Imta trys Ar/C₂H₂ dujų santykiai (100, 150 ir 200) ir dvi plazmos generatoriaus galios vertės – 600 ir 870 W. Dangos tirtos skenuojančiuoju elektroniniu mikroskopu, Ramano (RS) ir infraraudonųjų spindulių (IR) spektroskopijos metodais.

Nustatyta, kad didinant plazmos generatoriaus galią ir mažinant Ar/C₂H₂ santykį dangų augimo greitis sparčiai didėja (nuo 20 iki 425 nm/s), tačiau augant nusodinimo greičiui formuojasi koloninės struktūros ir netolygaus mikroreljefo dangos. Matavimai parodė, kad keičiant išlydžio parametrus ir nešančiųjų bei darbinių dujų san-

tyki, plazmos srauto temperatūra kinta 570–690 °C ruože. Taigi, keičiant darbinės sąlygas keičiasi acetileno disociacijos ir sintezės procesai, padėklą pasiekia nevienodi kiekiai skirtingos prigimties ir energijos radikalų. RS ir IR tyrimai parodė, kad naudotame išlydžio galių ir dujų santykių ruože gautos a-C:H dangos nebuvo vienalytės: jose yra deimanto tipo (sp^3) anglies, grafito tipo (sp^2) anglies ir stiklo anglies fazės. Argono–acetileno santykio didėjimas lemia sp^2/sp^3 ryšių kitimą dangoje, bet skirtingoms plazmos generatoriaus galioms tai vyksta nevienodai, pavyzdžiui, esant 600 W galiai, sp^3 ryšių koncentracija mažėja didinant Ar/C₂H₂ santykį, tuo tarpu esant 870 W sp^3 ryšių kiekis išauga mažinant acetileno kiekį plazmoje.