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# Deposition and structure characterization of carbon films prepared at atmospheric pressure by plasma jet

Liutauras Marcinauskas [a,b], Vitas Valinčius [a,*], Alfonsas Grigonis [b]

[a] Lithuanian Energy Institute, Plasma Processing Laboratory, Breslaujos 3, LT-44403 Kaunas, Lithuania
[b] Department of Physics, Kaunas University of Technology, Studentų 50, LT-51368 Kaunas, Lithuania

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ABSTRACT

Amorphous carbon films were deposited on stainless steel substrates by plasma jet chemical vapor deposition (PJCVD). The carbon coatings have been prepared at atmospheric pressure in an argon/acetylene mixture. The $Ar/C_2H_2$ gas volume ratio varied from 100:1 to 200:1, while the distance between the plasma torch nozzle exit and the samples was 0.005–0.02 m. Scanning electron microscope analysis demonstrated that the surface roughness and growth rate of the coatings increase with the decrease of the $Ar/C_2H_2$ ratio. The ERDA results showed that the hydrogen concentration rises from 5 at.% to 27 at.% with the increase of the distance from 0.005 to 0.02 m. The increase of the $Ar/C_2H_2$ ratio from 100:1 to 200:1 slightly increases the hydrogen and oxygen concentration in the films. The Raman spectroscopy results indicated that the $sp^3$ C–C carbon sites are replaced by $sp^3$ $CH_{2-3}$ bonds with the increase of the deposition distance. The microhardness of the carbon films deposited at 0.005 m was in range of 7.1–9.3 GPa.

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## 1. Introduction

The amorphous hydrogenated carbon films have attracted extensive attention due to their outstanding physical, tribological, and chemical properties like optical transparency, high mechanical hardness and elastic modulus, low friction coefficient, biocompatibility, and chemical inertness [1–3]. These properties make amorphous carbon coatings suitable for large variety of application field (biomedicine, tribology, microelectronics, optics, etc.) [1,2]. However, these outstanding properties and applications of a-C:H coatings are very strongly dependent on the atomic hydrogen content and ratio of $sp^2$ C=C bond to $sp^3$ C–C bonds [1–7].

Nowadays various deposition techniques (plasma-enhanced CVD [4,8], plasma-assisted CVD [3], magnetron sputtering [6], and ion beam-assisted deposition [7]) can be used to prepare a-C:H films. Each method has its advantages over others. The main advantages of plasma jet CVD are relatively high growth rates and the possibility to form carbon coatings at reduced and even atmospheric pressure conditions [9–15].

The experimental parameters (plasma torch power, hydrocarbon gas type and its amount, substrate temperature, deposition distance, etc.) during the formation of a-C:H films will directly affect the $sp^2$ to $sp^3$ carbon site fraction and hydrogen concentration [10–15]. The deposition distance and $Ar/C_2H_2$ ratio change the plasma jet composition and atomic hydrogen density in plasma flow. As a result the film microstructure and properties are different [11]. The torch power, substrate temperature, and precursor type also stipulate the various growth rates, hardness values, and hydrogen concentration values [10,13]. However, the research concerning the formation of carbon films at atmospheric pressure by the plasma jet technique is hard to find in the scientific literature. So it is very important to estimate the influence of various parameters on the structure of the carbon films.

In this study, we investigate the effects of the acetylene flow and plasma torch–substrate distance on the surface morphology, bonding type and structure of the amorphous carbon films prepared by the plasma jet technique.

## 2. Experimental setup

A direct current plasma torch was used to obtain the carbon films on stainless steel substrates at the atmospheric pressure. The 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 hydrocarbon gas introduction [14]. Argon (flow rate of 6.6 l/min) was used as a feed gas, and acetylene ($C_2H_2$) as a precursor (0.066–0.033 l/min). The steel substrates were polished and chemically cleaned with acetone and kept for 30 s in argon plasma before the deposition. The plasma torch power was ~600 W and the deposition time —120 s. The formation conditions and thickness of the produced carbon films are summarized in Table 1.

Scanning electron microscope (SEM) was used to analyze the surface morphology and through cross-sectional views the film thicknesses were measured. The plasma flow temperature above the substrate was measured by chromel–aliumel (X–A) thermocouple with an average

* Corresponding author. Tel.: +370 37 401896; fax: +370 37 351 271.
*E-mail address:* vitas@mail.lei.lt (V. Valinčius).

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**Table 1**
The deposition parameters of the carbon films.

| $Ar/C_2H_2$ volume gas ratio | Distance [m] | Plasma temperature [°C] | Thickness of the films [μm] | Growth rate [nm/s] |
|---|---|---|---|---|
| 200 | 0.005 | 920 | ~0.40 | $3.3 \pm 0.1$ |
| 200 | 0.01 | 570 | ~2.4 | $20 \pm 0.5$ |
| 200 | 0.015 | 370 | ~3.0 | $25 \pm 0.5$ |
| 200 | 0.02 | 260 | ~1.0 | $8.5 \pm 0.5$ |
| 100 | 0.005 | 1050 | ~0.50 | $4.2 \pm 0.1$ |
| 150 | 0.005 | 950 | ~0.450 | $3.75 \pm 0.1$ |

temperature error of ± 10 °C. The bonding structure of carbon films was measured using Raman scattering (RS) and Fourier transform infrared (FTIR) spectroscopy [14]. The depth distributions of elements were measured by Rutherford backscattering spectrometry (RBS) using a 2.0 MeV energy helium ions at a scattering angle of 165°. The hydrogen concentration was obtained by elastic recoil detection analysis (ERD), which was performed using a helium ($^4He^{+2}$) ion beam with 2.0 MeV energy and with 80° beam-incidence angle to the surface normal. The microhardness measurements were performed using a loading device (MTS Nanoindenter G200) with a squarebased Vicker's diamond pyramid as an indenter.

## 3. Results and discussions

The SEM results demonstrated that the surface of film deposited at 0.005 m is smooth (Fig. 1a). The growth rate increases with the increases of the deposition distance from 0.005 m to 0.015 m. Meanwhile the further increase of the distance (up to 0.02 m) decreases the deposition rate (Table 1). The surface of the films deposited at ≥ 0.01 m consists of the 100–500 nm size fragments, indicating an island growth mechanism (Fig. 1b). It was obtained that the deposition rate increases with the decrease of the $Ar/C_2H_2$ ratio. It also changes the surface of the coatings. The film prepared at $Ar/C_2H_2 = 150$ is uniform and covered by randomly distributed 100–500 nm grains, while the coating formed at $Ar/C_2H_2 = 100$ consists from the coalesced 500 nm size grains (Fig. 1c).

The RBS and ERD results demonstrated that the oxygen and hydrogen concentration increases with the increase of the distance for the films prepared at $Ar/C_2H_2 = 200$. The coating deposited at 0.005 m mainly consists of carbon (92 at.%) with a low concentration of oxygen (~3 at.%) and hydrogen (~5 at.%). While the film prepared at 0.02 m have up to 15 and 27 at.% of oxygen and hydrogen, respectively. The slight increase of the hydrogen and oxygen concentrations was obtained with the increase of the $Ar/C_2H_2$ ratio. The coating obtained at $Ar/C_2H_2 = 100$ has very low hydrogen (~2 at.%) and oxygen (~1 at.%) content. While the film deposited at $Ar/C_2H_2 = 150$ consists of 94 at.% carbon, 3 at.% hydrogen, and 3 at.% oxygen.

The microhardness measurements demonstrated that the coating deposited at $Ar/C_2H_2 = 100$ and 0.005 m shows the highest hardness value (9.3 GPa). With the increase of the $Ar/C_2H_2$ ratio the hardness decreases. The microhardness of the coatings prepared at $Ar/C_2H_2 = 150$ and $Ar/C_2H_2 = 200$ ratios are 8.5 and 7.1 GPa, respectively. Meanwhile the films deposited at $Ar/C_2H_2 = 200$ and distances ≥ 0.010 m are not harder than 0.5–1.0 GPa.

The Raman spectra of carbon films deposited at $Ar/C_2H_2 = 200$ and various distances, are presented in Fig. 2. The spectrum of the film prepared at 0.005 m consists of the two short-range intensity peaks; D centered at 1348 $cm^{-1}$ and G at 1617 $cm^{-1}$. The full width at half-maxima (FWHM) of the D band is 184 $cm^{-1}$ while the FWHM of the G peak is 58 $cm^{-1}$. The integral intensity ratio between the D and G peaks ($I_D/I_G$) of the film is 2.23. The narrow G peak indicates the graphite phase with nanocrystalline grains. The film obtained at 0.01 m has a D peak lain at 1410 $cm^{-1}$ (with a FWHM of 235 $cm^{-1}$) and G at 1617 $cm^{-1}$ (with a FWHM of 74 $cm^{-1}$). The $I_D/I_G$ ratio is increased up to 2.41. The

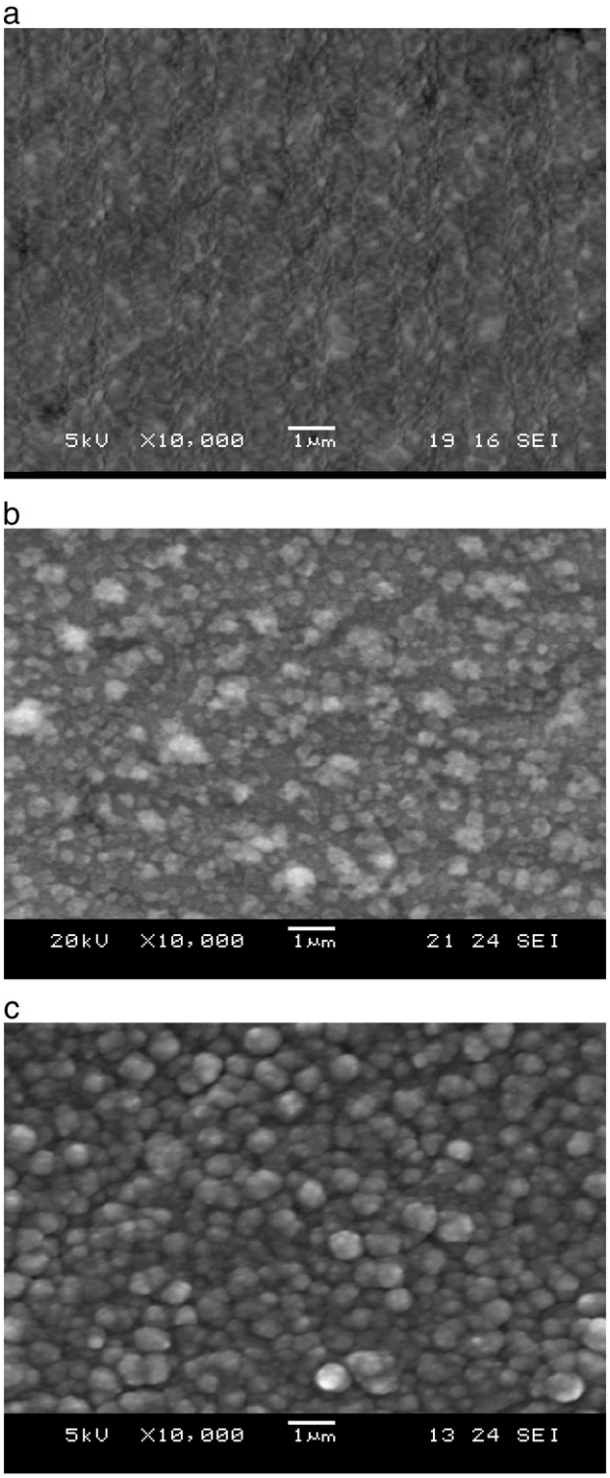


**Fig. 1.** The SEM images of carbon films (a) $Ar/C_2H_2 = 200$ and 0.005 m, (b) $Ar/C_2H_2 = 200$ and 0.02 m, (c) $Ar/C_2H_2 = 100$ and 0.005 m.

further increase of the deposition distances diminishes the D and G peak positions. The D peak is found at 1395 $cm^{-1}$ (FWHM is 203 $cm^{-1}$) and G at 1613 $cm^{-1}$ (FWHM is 86 $cm^{-1}$) for the coating prepared at 0.015 m. The $I_D/I_G$ ratio decreases down to 1.56. The film deposited at the highest distance shows the lowest (1.34) $I_D/I_G$ ratio. The uprising spectra also are related with a polymeric nature [1]. The positions of the D and G peaks of this coating are situated at 1388 $cm^{-1}$ and 1606 $cm^{-1}$, respectively. Meanwhile, the FWHM of the D and G bands is 187 $cm^{-1}$ and 97 $cm^{-1}$, respectively. The RS results demonstrated that the G peak positions slightly shift to lower values (from 1617 $cm^{-1}$ to 1606 $cm^{-1}$), while the

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