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Surface and Structural Analysis of Carbon Coatings Produced by Plasma Jet CVD

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Amorphous hydrogenated carbon films were deposited on Si (111) wafers from argon-acetylene gas mixture at atmospheric pressure by plasma jet chemical vapor deposition. The Ar / C_2H_2 gas volume ratio was 12 : 1, 60 : 1, and 100 : 1, while the distance between plasma torch nozzle exit and the samples was 0.01 m. Scanning electron microscopy analysis revealed that the growth rate and surface roughness of the coatings increases decreasing the Ar/C_2H_2 gas ratio. The Raman results show an increase of the sp^3 bond fraction with decrease of the acetylene gas in argon plasma. The Fourier transform infrared (FTIR) spectroscopy indicated that the films permeability increases with decreasing Ar/C_2H_2 ratio. It revealed that the surfaces roughness, growth rate, bonding structure, and optical properties of the carbon coatings depend on the Ar / C_2H_2.

Keywords: carbon coatings, plasma, acetylene, Raman spectroscopy.

INTRODUCTION

Nowadays, the interest on the carbon coatings (amorphous hydrogenated (a-C:H), hydrogen free (a-C)) and nanostructures (fullerenes, nanotubes, nanocones) in the practical application has drastically increased [1 – 3]. a-C:H films due to their unique properties, such as: low friction coefficients, high wear resistance, extremely high hardness, optical transparency, and chemical inertness are great candidates for protective coatings, optical, biomedical, electronic application [1].

Many different chemical vapor deposition (CVD) and physical vapor deposition (PVD) methods, such as: plasma enhanced CVD [4, 5], plasma jet CVD [6] magnetron sputtering [7], ion beam deposition [8], glow-discharge [9] are used to produce a-C:H films. The most of these techniques allows to obtain excellent quality a-C:H films, however the films growth rate is not sufficient. Among these methods, plasma jet CVD offers possibility to deposit polycrystalline diamond or amorphous hydrogenated carbon films at reduced or even at atmospheric pressure. The second advantage is high growth rate up to 70 nm/s, what usually is about 10 to 100 times faster than the growth rates achieved by others PVD or CVD techniques [6, 10 – 14]. However there is over the sixty different parameters that influence during the formation of films by plasma jet CVD. The main factors are pressure, plasma torch power, hydrocarbon gas content in plasma, precursors gas type and injection place, distance (plasma torch – substrate), substrate temperature, and etc. [6, 10 – 13]. Many authors investigated influence of these parameters on the carbon films properties, structure, and surface morphology at reduced pressure conditions. Although many researchers have proposed several mechanisms for carbon films growth during plasma jet CVD, the complete understanding of the actual mechanisms involved during coatings growth is still open for debate [6, 10]. Also most of the carbon coatings were produced using argon-methane or hydrogen-argon-methane gases plasmas. Meanwhile there is lack of information about carbon films structure, surface porosity, bonding type deposited from the argon-acetylene gas plasma at reduced or atmospheric pressure conditions.

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

EXPERIMENTAL

Coatings were deposited using a direct current (DC) plasma torch. The DC plasma torch consists of the copper cathode with the hafnium emitter, the working gas injecting ring with two tangential blowholes, and a step formed anode nozzle with blowhole for the precursor gases introduction. Both electrodes are cooled by water in order to prevent them from erosion caused by enormous heat flux from the arc. More details about the plasma torch can be found elsewhere [15]. An argon was a carrier gas, and acetylene (C_2H_2) as a precursor with flow rates of 0.12 l/s and $(0.12 – 1.00) \cdot 10^{-2}$ l/s, respectively. C_2H_2 was introduced into the anode and due to a high temperature of plasma dissociation process starts. Carbon coatings were formed on (111) silicon wafer substrates at atmospheric pressure, at a plasma torch – substrate distance of 0.01 m. The plasma torch power was ~820 W. Before deposition the silicon wafers were chemically cleaned by acetone and in the argon plasma for 30 s. Substrates were cooled by water during the plasma deposition operation. Process parameters and thickness of the coatings are presented in Table 1.

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Table 1. Preparation conditions of the carbon films

Ar / C_2H_2 volume gas ratio	12	60	100
Deposition time, s	300		
Film growth rate, μm/s	2.940	0.534	0.500
Plasma temperature above substrate, °C	480	930	980

Thickness and surface morphology were characterized by scanning electron microscopy (SEM) model JEOL JSM-5600. Optical properties and bonding structure of the carbon films were determined using FTIR and Raman scattering (RS) spectroscopy. The RS spectra were recorded by a conventional grating Raman spectrometer. For excitation of the Raman spectra argon ion laser, operating at 514.5 nm wavelength with 20 mV power was used. The overlapped background corrected Raman spectral bands were fitted with Gaussian contours, using least squares fitting software. The FTIR spectra were obtained using a Perkin Elmer spectrometer (model Spectrum GX FT-IR). FTIR reflectance and transmittance spectra were detected in the range of $670\ cm^{-1} – 4000\ cm^{-1}$ and $400\ cm^{-1}$ – $4000\ cm^{-1}$ respectively, at spectral resolution of $0.3\ cm^{-1}$ using an air and the silicon wafer as a reference. Plasma temperature in the vicinity of the substrate was measured by a chromel-aliumel thermocouple.

RESULTS AND DISCUSSIONS

The coatings growth rate (Table 1) and surface porosity (Fig. 1) increases with increasing acetylene flow in argon plasma. This is due to the higher amount of hydrocarbon particles available in plasma and this fact correlates with other authors results [6, 11]. For the film prepared at $Ar / C_2H_2 = 12$ is typical the column structure. The diameters of the columns vary from 50 μm to 100 μm. Each column consists of the branches with the size of 10 μm. Coatings deposited at higher Ar/C_2H_2 ratios are more uniform. Despites the column structure still dominates coalescence of the columns starts. The cross-section views show that the film deposited at higher argon-acetylene gas ratio has more dense structure. The columnar structure of the coatings indicates that the films are formed by an island growth mechanism.

Temperature measurements demonstrated an increase of the plasma temperature from 480 °C up to 980 °C with the decrease of acetylene flow. These results indicate that the plasma jet temperature and composition of dominant species in plasma can be changed by varying the acetylene gas flow. Benedikt [14] defined that at high acetylene flows dominant radicals in plasma are C_2H, C_3H_2, C_4H_2 and etc. With decreasing the acetylene flow, more C_2H_2 is fully decomposed into the H, C, C_2 or CH species. As a result, plasma jet temperature will rise and these species will be responsible for the production of a-C:H films.

As can been seen from Fig. 2, a, the film produced at the lowest Ar / C_2H_2 ratio show the highest transmittance value. An increase of the argon-acetylene ratio leads to production of the carbon coatings with the lower transmittance. It may be noted that absorption increases at the higher IR wave number range. Films deposited at the $Ar / C_2H_2 = 60$ and $Ar / C_2H_2 = 100$ are opaque to IR waves in the range of $1200\ cm^{-1} – 4000\ cm^{-1}$.

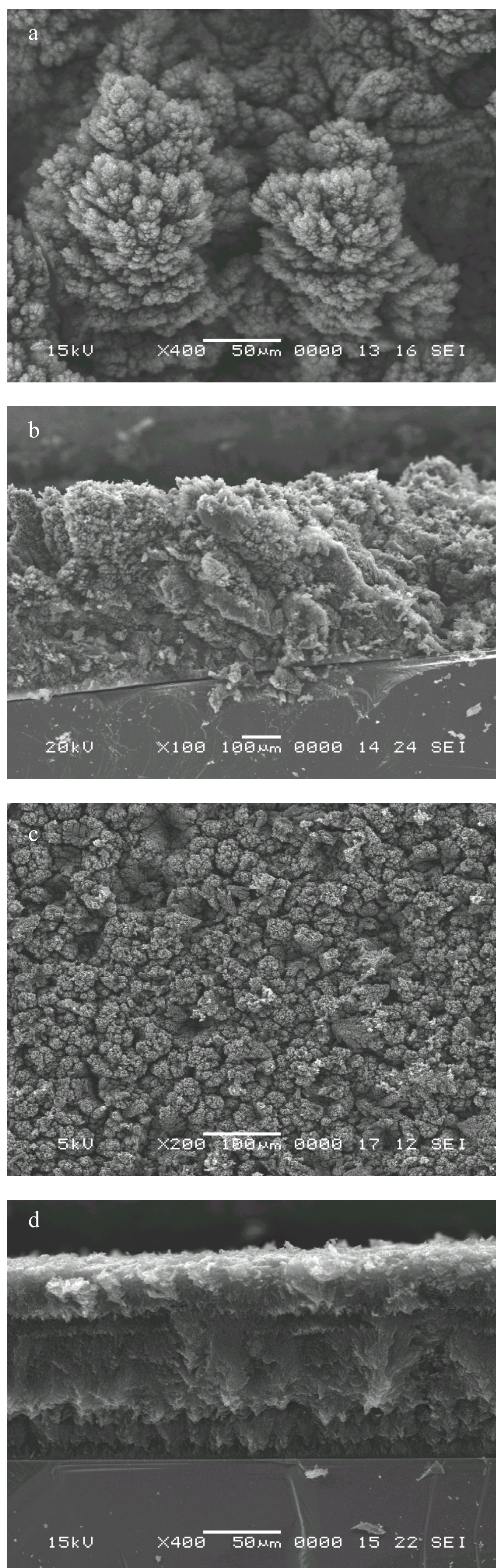

Fig. 1. SEM surface morphology (a, c) and cross-section (b, d) of carbon films deposited at various Ar/C_2H_2 ratios: a, b – $Ar / C_2H_2 = 12 : 1$; c, d – $Ar / C_2H_2 = 100 : 1$

The absorbance band centered at 1720 cm^{-1}, that is much more pronounced for the sample deposited at $Ar / C_2H_2 = 60$, indicates a contamination of carbon films by oxygen (C=O stretching range mode) [7]. The peaks found at 1600 cm^{-1} and 1250 cm^{-1} are ascribed to sp^2 C=C and sp^2/sp^3 C–C bonded carbon, respectively [1].

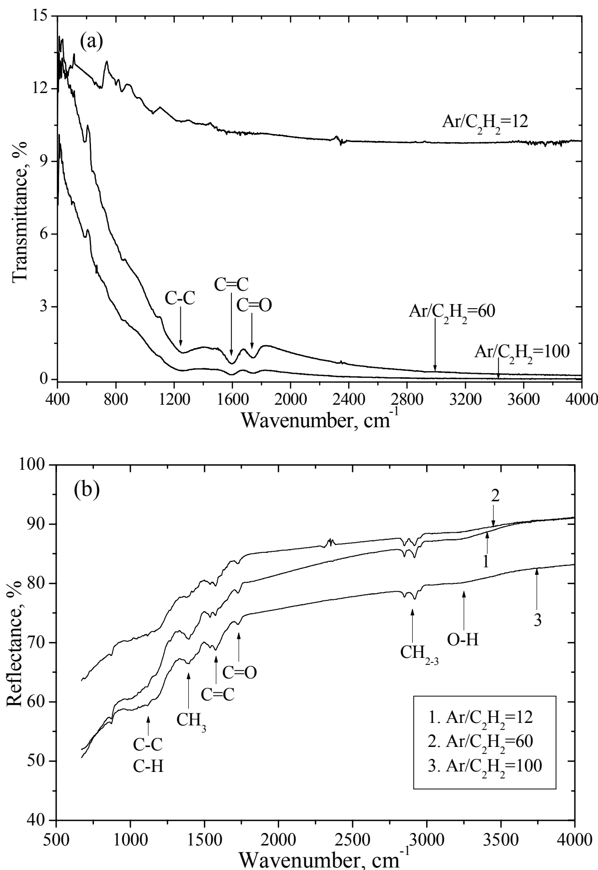

Fig. 2. FTIR transmittance (a) and reflectance (b) spectra of the carbon coatings formed at different Ar / C_2H_2 ratios

The reflectance spectra of all carbon films show the same character (Fig. 2, b). The absorption of the coatings decreases rapidly down to 20 % – 30 % in the range of 670 cm^{-1} – 1800 cm^{-1}, and slightly to 10 % in 1800 cm^{-1} – 4000 cm^{-1}. Existence of the wide band at 3100 cm^{-1} – 3400 cm^{-1} is attributed to OH bonds. However the width of this peak also indicates presence of the sp^1 CH sites in the films. The dominant absorption at 2850 cm^{-1} and 2920 cm^{-1} is related to sp^3 CH_2 symmetric and asymmetric stretch modes, respectively. The low intensity band at 2960 cm^{-1} is attributed to the asymmetric mode of sp^3 CH_3 sites [1, 7]. The peaks appearing at 1725 cm^{-1} and 1575 cm^{-1} indicate sp^2 C=O and C=C bonds, respectively. The sp^2 C=C band become more distinct and deeper with the decreasing acetylene flow. The width of the C=C peak demonstrates that carbon bonds are aromatic and olefinic configurations. Yi [16] supposed that this broadness is due to interaction between the C=C vibrations and the adjoining sp^2 C–H bonds. The absorbance band found at 1180 cm^{-1} is related to C–H, C–C or C–O groups. Presence of the C=O and O–H bands in the a-C:H films according to Louh [5] shows a large concentration of free radicals, which react with oxygen.

Raman spectrum of the carbon coating formed at $Ar / C_2H_2 = 12 : 1$ ratio does not indicate any typical peaks related to the carbon structures in the range of 1000 cm^{-1} – 1800 cm^{-1} (Fig. 3). According to the RS measurements we could not identify the structure of this film. As a remark, it may be noted that the coating could not be attributed to the amorphous graphite-like carbon (GLC) or diamond-like carbon (DLC) films. Meanwhile, the increase of the Ar / C_2H_2 ratio completely changes the structure of the carbon coatings. The RS spectrum of the film deposited at $Ar / C_2H_2 = 60 : 1$ consists from the two separated peaks attributed to well known D and G bands [1, 8]. To estimate the positions and full width at half-maxima (FWHM) of D and G peaks, the Gaussian fitting was done. It was found that D peak is located at 1381 cm^{-1}, while G band position is at 1604 cm^{-1}. The FWHM of G and D peaks are 85 cm^{-1} and 211 cm^{-1}, respectively. The positions of these bands compared to typical D and G peaks of the a-C:H films are shifted to the higher frequencies. According to Robertson [1] it is related with reduction of bond angle disorder and growth of graphite domains. The relative ratio of the D peak to G (I_D / I_G) is 1.92. The I_D / I_G ratio comparing to typical DLC films is high and shows that the relative fraction of sp^2 sites is higher than sp^3. Raman spectra shape indicated that this film could not be attributed to typical DLC or GLC coatings, due to domination of the right shoulder. The coating may have glassy carbon phase.

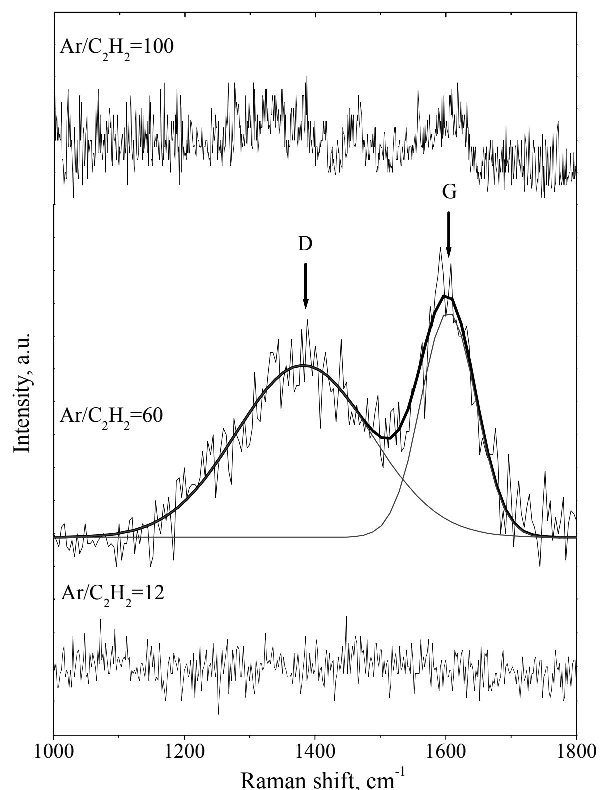

Fig. 3. Raman spectra of carbon coatings formed at various Ar / C_2H_2 ratios

The Raman spectra of the film deposited at the highest Ar / C_2H_2 ratio have three low intensity peaks around 1331 cm^{-1}, 1599 cm^{-1}, and 1450 cm^{-1}. The bands found at 1331 cm^{-1} and 1599 cm^{-1} are attributed to D and G peaks in

glass carbon, while the feature obtained at 1450 cm^{-1} is assigned to a C5 $A_{g(2)}$ "pentagonal pinch" mode [17].

RS and FTIR results indicated that films prepared at $Ar/C_2H_2 = 60$ and $Ar/C_2H_2 = 100$ consist of sp^2 C=C, C=O, sp^3 C–C, C–H (in CH_{2-3}) bonds. The experimental results demonstrated that decrease of acetylene in argon plasma influences the growth of sp^2 and sp^3 sites fraction. Zaharia et all [11] assumed that the sp^3 fractions are high for relatively lower C_2H_2 flow. However in this case sp^3 bond comes from polymeric C–H bonds, due to the hydrogen incorporation in the films. As the C_2H_2 flow increases, the total sp^3 fraction decreases due to reduction of the hydrogen in the coatings. Neyts [18] in the molecular dynamics simulation showed that at low influx of acetylene, a film will have a rather higher fraction of fourfold coordinated carbon atoms and higher hydrogen concentration in the film. The results can be explained in terms of the different growth mechanisms, as well as the growth species and their fluxes towards the substrate. The more carbon added to the film comes from particles that have no double or triple bonds (C, CH) at higher Ar/C_2H_2 ratios. Meanwhile, the C_2H radical becomes dominant growth species with the increase of the acetylene flow. Considering this, the coatings formed at lower Ar/C_2H_2 ratios will have more sp^1 and sp^2 sites. The experimental results show that films deposited even at $Ar/C_2H_2 = 100$ still have significantly high sp^2 fraction. This is due to the growth of graphitic domains due to the release of more H with the increasing plasma jet temperature.

CONCLUSIONS

Amorphous hydrogenated carbon coatings have been obtained using acetylene as a precursor gas at atmospheric pressure by plasma jet CVD. The coatings growth rates varied from 0.5 μm/s up to ~3.0 μm/s with the decrease of the Ar/C_2H_2 ratio from 100 to 12. It was observed that the growth rate and the surface roughness decreases with the decrease of the acetylene gas flow. Columned structure of the films indicated that coatings formation is stipulated by an island growth mechanism. FTIR and RS measurements demonstrated that the decrease of the acetylene flow leads to higher fraction of the sp^2 and sp^3 sites in the films. It was found that film deposited at $Ar/C_2H_2 = 60$ is amorphous DLC/GLC film with glassy carbon inserts, while coating formed at $Ar/C_2H_2 = 100$ consists of the mixed regions of sp^2 and sp^3 phases and five membered rings.

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