Deposition of Amorphous Hydrogenated Carbon Coatings by Plasma Jet

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In this study amorphous hydrogenated carbon films (a-C:H) were formed on Si (111) from an Ar–C_2H_2 and Ar–C_2H_2–H_2 gas mixtures at 1000 Pa pressure using a plasma jet chemical vapour deposition. It is shown that by varying the Ar:C_2H_2 ratio and adding the hydrogen gas in plasma, the structure, surface morphology, growth rate of the coatings, and consequently their optical properties can be controlled.

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1. Introduction

During the last decade the interest in the carbon films (amorphous hydrogenated (a-C:H), hydrogen free (a-C)), and nanostructures (nanotubes, fullerenes), their deposition, investigation of their properties, and practical application has considerably increased [1–3]. a-C:H films due to the specific optical properties such as: optical band gap (1.1–4.0 eV), refractive index (1.5–3), transmittance and reflectance in infrared region (they all vary in a wide range of values) are candidates for the electronic application (as field effect transistors, micro-elecromechanical devices (MEMs)) [1, 2].

In this paper an experimental work was done to investigate effects of various argon/acetylene ratios and introduction of an additional hydrogen on the optical properties and structure of carbon coatings.

2. Experimental setup

Carbon coatings were produced on silicon (111) substrates at 1000 Pa pressure using a linear direct current plasma torch. More details about the plasma

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torch and deposition process can be found elsewhere [4]. Argon (Ar) and hydrogen (H_2) were the plasma working gases, with flow rates of 0.144 l/s and 0.058 l/s, respectively. Acetylene (C_2H_2) was used as precursor with various flow rates 0.018–0.144 l/s. Silicon wafers were chemically cleaned by acetone and in an argon plasma before starting the deposition process, samples being cooled by water during deposition. Distance plasma torch — substrate was 0.06 m, coatings deposition time — 300 s.

Surface morphology was characterised by scanning electron microscopy (SEM) model JEOL JSM-5600. Bonding structure and optical properties of carbon films were characterised using FTIR spectrometer (GX FT-IR) and Raman scattering (RS) spectroscopy. Electron paramagnetic resonance (EPR) analysis was done using an E/X-2547 spectrometer.

3. Results and discussion

It was founded that increase in the acetylene gas amount in argon plasma leads to more dense and relatively smoother surface morphology. Introduction of the additional hydrogen in argon plasma allows to decrease porosity of the carbon film (see Fig. 1); however, the growth rate also decreases, because the hydrogen intensively etches the graphitic phase. The coatings consist of grains adhered and fused together into aggregates, although the individual micro-grains are still distinguishable.
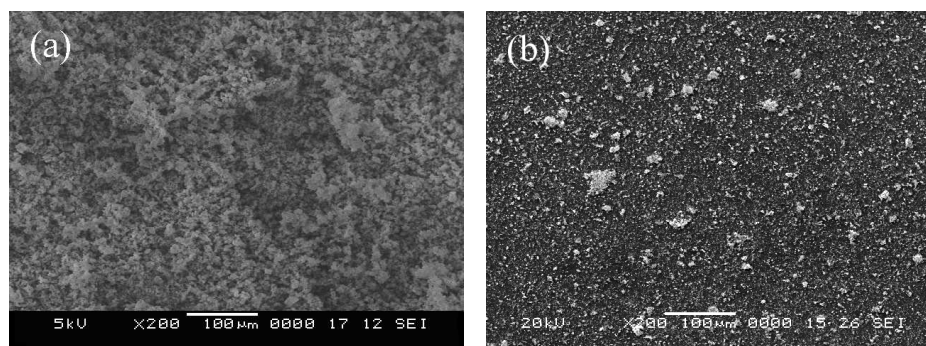

Fig. 1. Surface morphology of carbon coatings deposited at (a) $Ar/C_2H_2 = 5 : 1$, (b) $Ar/H_2/C_2H_2 = 5 : 2 : 1$.

FTIR reflectance spectra of the coatings prepared at $Ar/C_2H_2 = 8 : 1$ and $Ar/C_2H_2 = 5 : 1$ ratio are comparable, while the reflectance of the coating obtained at $Ar/C_2H_2 = 1 : 1$ in the frequency range of 670–1800 cm^{-1} is considerably lower (up to 20%). It was found that the intensity of the OH and sp^1 C–H peaks in the 3000–3600 cm^{-1} range broadened with increasing acetylene gas flow. Meanwhile, film deposited with additional hydrogen ($Ar/H_2/C_2H_2 = 5 : 2 : 1$) shows the highest reflectance values.

Figure 2a shows that decrease in the Ar/C_2H_2 ratio leads to widening of the OH and sp^1 C–H bonds peaks. Due to this very broad band it is difficult to determine the absorption bands related with the sp^3 CH_{2-3} vibrations in the 2850–3000 cm^{-1} range for the film deposited at $Ar/C_2H_2 = 1:1$ [1]. The bands with absorption maximum at around 1700 cm^{-1} and 1250 cm^{-1} in the IR spectra of carbon films are attributed to the sp^2 C = O stretching and mixed sp^2/sp^3 C–C bonds [1, 5]. The intensity of these peaks become more prominent when the Ar/C_2H_2 ratio is increased, while the peak at 1600 cm^{-1} corresponding to sp^2 C = C bond remains almost unaltered. A small intensity peaks around 2850 cm^{-1} and 2930 cm^{-1} indicate the sp^3 methylen (CH_2) symmetric and asymmetric stretching modes, respectively, while the band at 2960 cm^{-1} is due to sp^3 CH_3 asymmetric stretching bonds. Presence of sp^3 C–H bonding in the film obtained at $Ar/C_2H_2 = 8:1$ is further confirmed by the peaks at 1370 cm^{-1} and 1440 cm^{-1} which are the modes associated with the bending of the CH_3 bonds (Fig. 2a, curve 3) [1]. The existence of the broad band at the 3000–3600 cm^{-1} frequency for the coating obtained at $Ar/C_2H_2 = 1:1$ leads to suggestions that the most of the carbon are bonded with the hydrogen due to sp^1 bonds (Fig. 2a, curve 1). This means that coating mainly consists of the C_2H_2, ethinyl, or heavier radicals. The film prepared with additional hydrogen shows deep absorption band at 1580 cm^{-1}, representing aromatic sp^2 C = C bonds, and small intensity peaks indicating sp^3 CH_{2-3} bonds. Film transparency increases if the hydrogen gas is added during the deposition (Fig. 2a, curves 2 and 4).
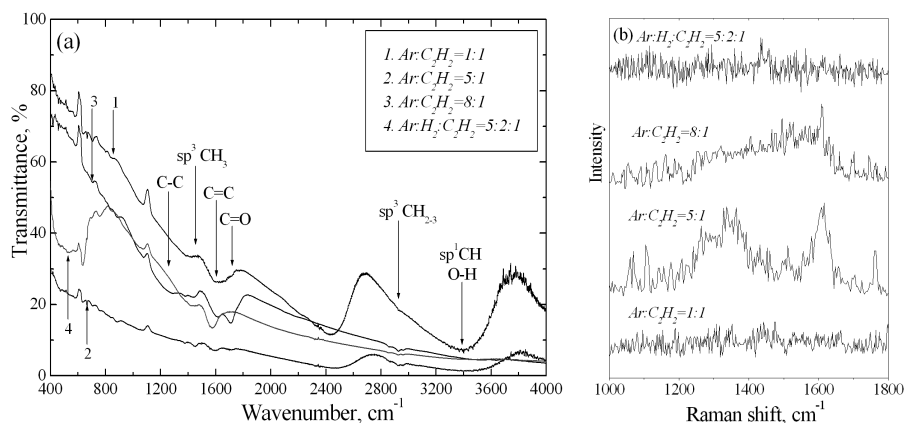

Fig. 2.   FTIR transmittance (a) and Raman (b) spectra of carbon coatings.

The Raman spectra of carbon coatings deposited at $Ar/C_2H_2 = 1:1$ and $Ar/H_2/C_2H_2 = 5:2:1$ do not show signal in the range of 1000–1800 cm^{-1}. The coating prepared at $Ar/C_2H_2 = 5:1$ ratio consists of the two short-range intensity peaks; D centred at 1336 cm^{-1} and G at 1608 cm^{-1} (Fig. 2b). The full width at half-maxima (FWHM) of the G (≈ 70 cm^{-1}), and D (≈ 100 cm^{-1}) bands, also the

position of G peak indicates formation of the graphite phase with a small grain size of nanocrystalline and high internal stresses in the coating [1]. A shape of the Raman spectra and insignificant dominating of the D peak resembles to glassy carbon films. The RS spectrum of the coating deposited at $Ar/C_2H_2 = 8 : 1$ consists of the G and D bands located around ≈ 1572 cm^{-1} and ≈ 1398 cm^{-1}, respectively. FWHM of the G peak is 120 cm^{-1} and 231 cm^{-1} for D. The ratio of I_D/I_G intensities is approximately 1.42.

The observed results clearly indicate that increase in the acetylene flow in the plasma will lower the plasma temperature and prevent the dissociation processes. At low acetylene flow enough argon ions and electrons survive the first charge transfer reaction between acetylene and argon ion followed by dissociative recombination (DR) of acetylene ion with electron and, thus, the remaining argon ions can react with the C_2H radical dominantly formed in the first DR step. For this reason the highest H, C, CH and C_2 concentration is at low acetylene flows [6]. Due to this with increasing Ar/C_2H_2 ratio and so with changing plasma composition, the hydrogen concentration goes up, leading to the formation of the glass carbon phase for the coating deposited at $Ar/C_2H_2 = 5 : 1$ and to growth of diamond-like carbon (DLC) a-C:H film at $Ar/C_2H_2 = 8 : 1$. EPR and FTIR measurements confirmed that dissociation processes in plasma slow down at higher C_2H_2 flow rates. The EPR signal ($g = 2.0028$) appropriate for DLC films was found only in film obtained at $Ar/C_2H_2 = 8 : 1$ and is in good correlation with RS results. Meanwhile, introduction of the additional hydrogen changes the nature of the EPR centres and leads to polymer-like carbon film formation.

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