FORMATION OF CARBON NANOSTRUCTURES USING ACETYLENE, ARGON-ACETYLENE AND ARGON-HYDROGEN-ACETYLENE PLASMAS

Liutauras Marcinauskas1(2), Alfonsas Grigonis1, Vitas Valnicius2, Virgilijus Minialga1

1) Kaunas University of Technology, Studentu 50, LT-51368, Kaunas, Lithuania, tel:+370 611 17031, fax:+370 37 456472, e-mail: liutauras.marcinauskas@ktu.lt
2) Lithuanian Energy Institute, Breslaujos 3, LT-44403, Kaunas, Lithuania, tel:+370 611 17031, fax:+370 37 351271, e-mail: liutauras@mail.lei.lt

The amorphous carbon films were deposited on silicon-metal substrates by plasma jet chemical vapor deposition (PJCVD) and plasma enchanted CVD (PECVD). PJCVD carbon films have been prepared at atmospheric pressure in argon-acetylene and argon-hydrogen-acetylene plasma mixtures. The films deposited in Ar-C2H2 plasma are attributed to graphite-like carbon films. The formation of the nanocrystalline graphite was obtained in Ar-H2-C2H2 plasma. Addition of the hydrogen gas lead to the decrease of growth rate and the surface roughness of the coatings. The carbon nanotubes were obtained by PECVD using gold-chromium catalyst particles at low (≤ 450°C; p = 40 Pa) temperature in pure acetylene plasma.

Introduction
There has been considerable interest in the last three decades in amorphous (non-hydrogenated and hydrogenated) carbon coatings and carbon nanostructures (nanotubes, nanoonions, carbon black, fullerene and etc.) due to their unique mechanical, chemical, optical and electrical properties. These fascinating properties make the carbon nanostructures great candidates for application in a wide variety of fields such as biochemical, biomedical, electronic [1,2]. Various deposition techniques are used to produce carbon films and nanostructures. It was shown that the synthesis temperature and characteristics of the catalyst play a key role in controlling the structure of carbon nanostructures [2-4]. Also the type of hydrocarbon gas and its amount, pressure have effect on final properties of deposited films. The use of acetylene gas as precursor instead of methane allows to reach higher growth rates [5-6]. However the information about the studies concerning the deposition of the carbon structures from the acetylene gas under the atmospheric pressure is not enough.

In this paper graphite nanostructures were fabricated from acetylene gas at 40 Pa and at atmospheric pressures. Experimental work was done to investigate the effect of various acetylene gas flow and temperatures on the carbon structure formation.

Experimental
The carbon films were formed on silicon-metal substrates by plasma PJCVD and PECVD. PJCVD carbon coatings have been prepared from Ar-C2H2 and Ar-H2-C2H2 plasma in atmospheric pressure. Argon gas flow rate was 6.6 l/min, hydrogen gas flow rate - 0.06÷0.24 l/min. These gases were used as feed gases, while acetylene (0.033÷0.066 l/min) as a precursor [5]. The distance between plasma torch nozzle exit and the samples was in the range of 0.005÷0.01 m. The carbon nanotubes were formed using acetylene gas (flow rate 4.16 cm³/s) at 40 Pa pressure. The deposition time was 60 s, distance 0.01 m, substrate temperature 450 °C. Emissive species in the argon-acetylene and argon-hydrogen-acetylene plasmas are studied in the 250–800 nm range by optical emission spectrometer (IFUAOS4).

PECVD carbon films have been prepared at ~ 40 Pa pressure in pure acetylene plasma. Surface morphology was analyzed by scanning electron microscopy (SEM). An elemental composition of the deposited thin films determine by energy-dispersive spectrometry (EDS). The bonding structure and optical properties were measured by Fourier transform infrared (FTIR) and Raman scattering spectroscopy. RS was investigated using Spectra – Physics YAG: Nd laser (532.3 nm, 50 mW, spot size 0.32 mm).

Results and Discussion
The spectra and assignment of different lines of argon-acetylene plasma are shown in Fig. 1. The line observed at 431.2 nm corresponds to the CH radical, specifically the Q-branch of the (0, 0) transition in the A'Δ–X'Π1 system. The main emission lines in argon-acetylene plasma are assigned to C2 swan D'Π1–A'Π1 [7]. When the hydrogen gas was used the OES plasma spectra shows the same species and radicals in the plasma. However compared to argon-acetylene plasma the argon-hydrogen-acetylene plasma OES spectrum demonstrates higher intensity of CH radical lines. So it indicates the increase of CH species in the plasma.

The SEM measurements indicated that films deposited using argon-acetylene plasma are rough and consist of columnar structure (Fig. 1). The columns diameters vary in the range of 5-10 µm. The each column consists of 500 nm size particles agglomerated to the bigger size fragments. The films growth rate decreased, oxygen concentration and sp² sites fraction increased with decreasing C2H2 flow rate. The surface roughness and growth rate of the graphite films decreases with introduction of the hydrogen and with the increase of H2 flow rate. The EDS measurement results demonstrated that films prepared without the hydrogen have low fraction of oxygen (~5 at.%). The addition of hydrogen gas lead to the of increase of the oxygen fraction up to ~10 at.%.

The films prepared in Ar-C2H2 plasma at high temperature (800–1200 °C) are attributed to graphite-like carbon films with significant fraction of sp² C-C sites. The synthesis of the nanocrystalline graphite was obtained in Ar-H2-C2H2 plasma. The RS results...
Fig. 1. The optical emission spectra of argon-acetylene plasma

Fig. 2. Surface morphology of carbon film deposited in argon-acetylene plasma

demonstrated that the variation of the hydrogen gas and temperature allows to change the sp² sites fraction. The formation of carbon nanostructures of 1-2 μm length and up to 200 nm diameters were obtained using argon-hydrogen-acetylene plasma on Si-Ni and Si-Au substrates. However the production of carbon nanostructures very strongly depends on the plasma gas composition and substrate temperature. The variation of the technological parameters allows changing the IR reflectance values of carbon films in wide range.

Fig. 3. Surface morphology of structures formed using acetylene plasma

It was found that the formation of the carbon nanotubes begins on the Si substrate covered by Au/Cr nano-islands in pure acetylene gas plasma at ~450 °C temperatures. The diameters of carbon nanotubes was in the range of 20 - 40 nm and the length up to 200 nm (Fig.3).

Conclusions

The films prepared in argon-acetylene plasma are attributed to graphite-like carbon films. Addition of the hydrogen decreases growth rate and the surface roughness of the films and lead to the formation of nanocrystalline graphite. The carbon nanotubes were formed at low (≤ 450 °C; p = 40 Pa) temperature in pure acetylene plasma.

References