Optical and Acoustical Methods in Science and Technology

Investigation of H_2:CH_4 Plasma Composition by Means of Spatially Resolved Optical Spectroscopy

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The system based on spatially resolved optical emission spectroscopy dedicated for *in situ* diagnostics of plasma assisted CVD processes is presented in this paper. Measurement system coupled with chemical vapour deposition chamber by dedicated fiber-optic paths enables investigation of spatial distribution of species densities (H_x, H^+, CH, CH^+) during chemical vapour deposition process. Experiments were performed for a various gas inlet configuration at range of microwave power up to 800 W. Spatially resolved optical spectroscopy results showed that inlet configuration based on injecting hydrogen in ECR region and methane in substrate area is the most efficient for H^+ and CH_3^+ excitation. The designed prototype of the spatially resolved optical spectroscopy system enables the high-sensitivity measurements of concentration of the species in the microwave plasma and can be used for optimisation of diamond-like carbon synthesis.

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1. Introduction

The advantages of thin diamond-like carbon (DLC) and diamond films make them promising material for optoelectronics (e.g. UV photodiodes and LEDs, protection coatings for the infrared optics) [1] and microelectronics (e.g. FET transistors, high frequency Schottky barrier diodes) [2].

However, the average growth rate of DLC layers synthesised by microwave plasma assisted chemical vapour deposition (μPACVD) processes is still unsatisfactory (≈ 1 μm/h) [3]. Moreover, the DLC layers often contain defects and inhomogeneities of the structure. These factors significantly limit the areas of their applications.

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The results of molecular dynamics calculation show that replacing of inactive particles (e.g. H_2, H, CH_3) at the growth surface by ions (e.g. H^+, CH_3^+) should increase growth ratio of the films [4]. Thus, the spatially resolved optical emission spectroscopy (SR-OES) was used to investigate whether H_2 molecules are dissociated and H^+ ions are produced in the plasma. OES technique enables non-invasive and remote measurements of plasma emission at the range of wavelength from UV up to IR.

The optical emission spectroscopy is based on Bohr's theory, where it is stated that the atom has a number of discrete energy levels related to the orbits of the electrons. These energy levels are the spectral terms. For an atom with a nucleus charge Z and one valence electron, the energy of this electron is given by

$$E = -\frac{2\pi Z^2 e^4 m\mu}{n^2 h^2}, \tag{1}$$

where m is the mass of the electron and M — the mass of the nucleus; n is the main quantum number ($n = 1,\ 2,\ 3,\ \ldots$) and gives the order of the energy levels [5].

As long as an electron is in a defined orbit no electromagnetic energy is emitted but when a change in orbit occurs, another energy level is reached and the excess energy is emitted in the form of electromagnetic radiation. In our case the change in orbit is mostly result of microwave radiation absorption and collision with electrons. The wavelength of emitted radiation is determined by Planck's law. Spectral analysis of emitted radiation enables identification of excited species and calculation of their energy levels. This phenomenon and non-invasiveness of method is essentially valuable for plasma analysis during diamond-like carbon synthesis [6]. It enables investigation of hydrogen and methane excitations levels and measure of plasma temperature.

2. Experimental

The spectroscopic experiments were performed in a stainless, water-cooled PA CVD system. The system consists of the pumping stage (a turbomolecular pump outfitted in a rotary and Root's pumps), microwave section, dc magnetic field section, gas channel and vacuum chamber. Microwave radiation (2.45 GHz) generated by a magnetron and dc magnetic field produced by two toroidal coils (3 kW power each), are involved together into electron cyclotrone resonance (ECR). Plasma composition measurements were carried out as a function of input microwave power up to 800 W at 100 sccm of H_2:CH_4 (99%:1%) gas mixture flow. The base pressure during the experiments was equal to 0.1 Pa.

Previous works showed that one-point OES plasma monitoring is insufficient in described CVD system because of highly non-linear influence of ECR effect [7, 8]. Although plasma composition can be investigated in selected area, excitation progress cannot be wholly monitored so its efficiency cannot be optimised. Thus, improvement of OES technique enabling spatially resolved measurements is required. Spanos et al. describe the methods dedicated for spatial distribution monitoring of excitation [9]. However, they are complex and time-consuming one as well as require the large viewport in the chamber. Therefore, author suggests to measure plasma composition only at the most important regions for DLC synthesis. Selection of these regions was based on analysis of gas inlet configuration and results of 3-dimensional magnetic field modelling. Such an approach simplifies optical setup and decreases amount of spectral data.

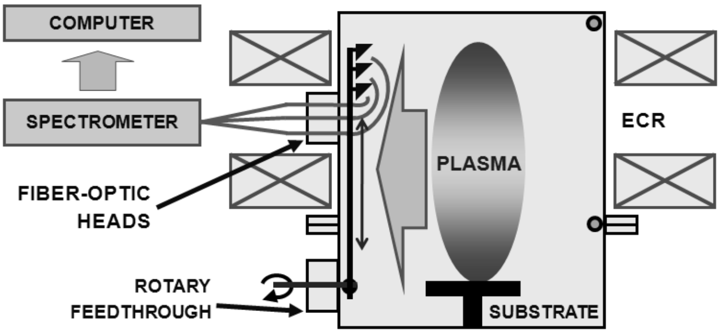

Fig. 1. Spatially resolved OES system coupled with the CVD chamber.

The spatially resolved OES system consists of fibre-optic heads, optical feedthrough and spectrometric detection part (see Fig. 1). The optical heads are mounted inside the chamber on the special linear translation rail. The position of the head is tuned by the automatic rotary motion drive along the longer axis of the chamber. The head was built using parabolic off axis mirror (diameter of 25 mm and angle of 90°), which couples the optical signal into the fibre bundle. The optical signal obtained from the head is transmitted through feedthrough and fibre cable to the spectrometers. A spectroscopic system (Monolight 6800 and Mechelle 900), working in wavelength range from 400 to 5000 nm with spectral resolution up to 0.3 nm, was used for detection of emission spectra. Dedicated software package was prepared for analysis of the spatial composition of species in plasma and the visualisation of scanning results.

3. Results

Intensity of emission lines at ECR region and substrate region was investigated to obtain information about spatial distribution of plasma excitation. Figure 2 shows examples of optical emission spectra obtained for H_2:CH_4 microwave plasma at different chamber regions. The spectral lines used to analyse of gas phase species and radicals are labelled in Fig. 2 and enumerated in Table [10].

Gas mixture (H_2:CH_4; 99%:1%) was being injected into the chamber in three different configurations: (I) mixture into ECR region; (II) mixture into substrate region and (III) hydrogen into ECR region while methane into the substrate region.

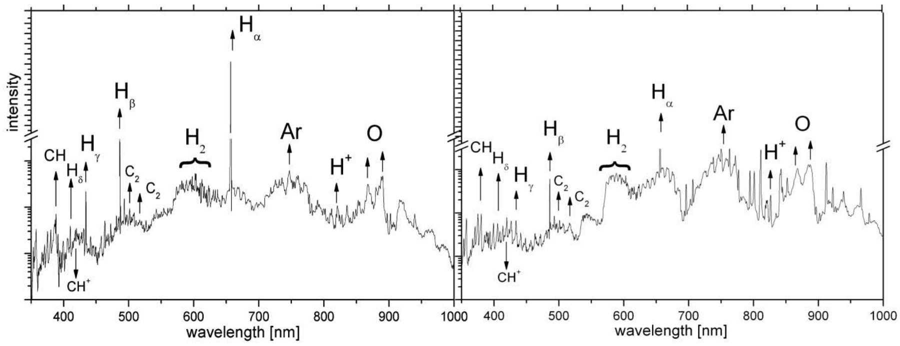

Fig. 2. Emission spectra of the H_2:CH_4 (99%:1%) plasma at ECR region (a) and substrate region (b) of chamber.

TABLE

Optical emission line analysed for the mixture of H_2:CH_4.

Species	Transition	Peak position [nm]
H_β	Balmer $n = 4 \rightarrow n = 2$	486.1
H_γ	Balmer $n = 5 \rightarrow n = 2$	434
H_δ	Balmer $n = 6 \rightarrow n = 2$	410
H_2	$G^1\Sigma_g \rightarrow B^1\Sigma_u$	462.9
H^+	Paschen $n = \infty \rightarrow n = 3$	820
CH	$B^2\Delta \rightarrow X^2\Pi$	387
CH^+	$A^1\Pi \rightarrow X^1\Sigma$	417.1
C_2	Swan $D^3\Pi_g \rightarrow A^3\Pi_u$	516.3

Two emission spectra shown in Fig. 2 were collected by SR-OES in gas (III) inlet configuration at ECR region (a) and substrate region (b). The intensity ratios related to H_β were used to overcome various excitation conditions. The evident difference of spectral lines intensity can be noticed. The decrease in the Balmer series lines and lower methane radical lines at substrate region are obtained.

The OES intensity ratios of most important species demonstrate strong influence of gas mixture inlet configuration. The intensities variations of main emission lines in function of gas configuration were presented in Fig. 3. Regarding the film growth ratio optimisation the spectral lines intensities of H^+ and CH_3^+ at substrate region were exactly analysed. The atomic hydrogen line P_∞ at 820 nm confirming dissociation and ionisation of hydrogen molecules up to H^+ achieve the highest level in (III) gas configuration. The strong decrease in the Balmer series lines and methane lines at substrate region is noticed. Such the effects reflect the increase in energy levels of hydrogen species and collisions with the methane radicals. However, the low level of spectral lines correlated to methane: CH (387 nm), CH^+ (417 nm) and C_2 (501, 516 nm) at substrate region were achieved. The production of these lines suggests presence of CH_3^+ radicals in plasma at the substrate region. These radicals play the most important role in nucleation processes of diamond-like carbon films.

The lowest decrease in all ratio intensities was observed in (III) gas configuration. It suggests that this gas configuration is the most efficient for H^+ and CH_3^+ excitation means DLC films synthesis.

The influence of microwave power on the emission intensities ratio of lines (H_x, P_∞, C_2, CH) was also studied.

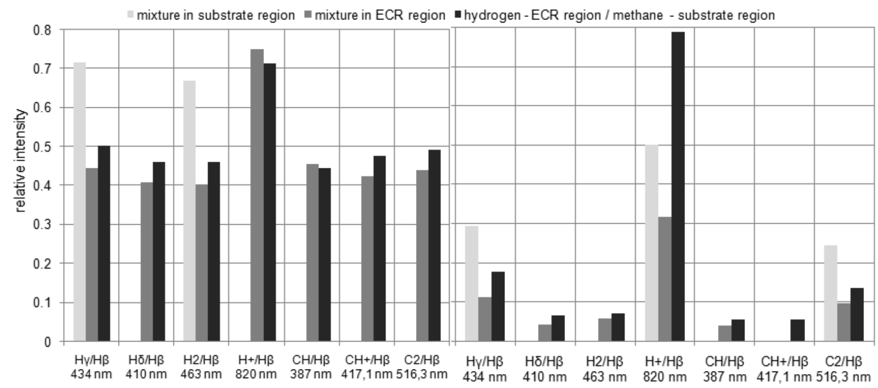

Fig. 3. Ratio of optical emission intensities of H_2:CH_4 (99%:1%) plasma at ECR region (a) and substrate region (b) of chamber.

It was observed that all ratios exhibit linear increase in function of higher microwave power. However, possibility of increase in microwave power is limited by subsequent increase in free electron energy, which can cause DLC film phase defects and structure destruction. It can be concluded that further SR-OES investigation should be supported by simultaneous *in situ* monitoring of the growing layer.

4. Conclusion

The use of SR-OES system gives significant amount of information about excitation process. Preliminary measurements made at two chamber sections show serious spatial variations of plasma composition. SR-OES results showed that hydrogen at ECR region and methane at substrate inlet configuration is the most efficient for H^+ and CH_3^+ excitation. It was also presented that the densities of H^+ and CH_3^+ strongly depend on microwave power level. Decrease in species densities at substrate section suggests that substrate stage should be shifted closer to ECR region. The obtained results showed that the designed prototype of the OES system enables the high-sensitivity measurements of concentration of the species in the microwave plasma. Fibre-optic system was upgraded to movable optical head to investigate other sections of plasma. Results of SR-OES monitoring will be applied as input parameters in the Carr–Parinello *ab initio* molecular dynamics calculations.

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