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Optoelectronic system for monitoring of thin diamond layers growth

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Development of the optoelectronic system for monitoring of diamond/DLC (Diamond-Like-Carbon) thin films growth during μPA ECR CVD (Microwave Plasma Assisted Electron Cyclotron Resonance Chemical Vapour Deposition) process is described. The multi-point Optical Emission Spectroscopy (OES) and Raman spectroscopy were employed as non-invasive optoelectronic tools. Dissociation of H_2 molecules, excitation and ionization of hydrogen atoms as well as spatial distribution of the molecules became subjects of the OES investigation. The most significant parameters of the deposited film like molecular composition of the film (ratio of diamond sp_3, graphite sp_2 and amorphous phases), presence of defects and rate of the film growth can be investigated by means of Raman spectroscopy. Modular Raman system for *in-situ* monitoring of the film growth, equipped with fibre probes, was designed. Investigation with use of optoelectronic tools provides important data about CVD process progress as well as enables optimization of DLC synthesis parameters and improvement of synthesized films quality.

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1. Introduction

Thin DLC and diamond layers are interesting materials, because of their extraordinary properties: electric (low dielectric function, wide energy band gap, high resistivity), optical (wide range of transmission) and thermal (high thermal conductivity). These advantages enable their applications in the optoelectronics (e.g. UV photodiodes and LEDs, protection coatings for the infrared optics) [1,2], microelectronics (e.g. semiconductors with the wide energy gap, FET transistors, high frequency Schottky Barrier Diodes) [3,4] and in other areas (e.g. sliding layers)[5].

The average growth rate of DLC layers synthesised by PACVD (Plasma Assisted Chemical Vapour Deposition) processes is still unsatisfactory (~1 μm/h) [6]. The DLC layers often contain defects and inhomogeneities in the structure. These factors significantly limit the areas of optical and microelectronic application.

The most studies of DLC processes consists of macroscopic parameters measurement such as microwave power, magnetic induction, gas flow and base pressure and then analyses of the influence of these parameters on the layer composition and the growth rate [7,8,9]. This approach is inadequate, because macroscopic process parameters can not be changed independently [10], so their influence on the layer quality can not be analyzed separately.

In this study the novel molecular approach of diamond layer growth optimization is proposed. Only few papers on analysis and molecular dynamics modelling of low-pressure growth of diamond have been published to date. Frenklach *et al.* [11] proposed the radical model of growth mechanism, while Tsuda *et al.* [12,13] assumed that not only radicals, but also ions participate in reaction of carbon atoms on the growth surface. Thus, the first step of investigation was calculation using molecular dynamics (hamiltonian AM1 and *ab initio*). The results 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 film [14,15] .

In second step, the *in-situ* optoelectronic system was developed to investigate molecular composition of the plasma and layer structure. The multi-point Optical Emission Spectroscopy (OES) was used to measure amounts of dissociated H_2 molecules and ionized H^+ ions inside the CVD chamber. Raman spectroscopy was applied to study molecular composition of films (ratio of diamond sp_3, graphite sp_2 and amorphous phases), content of defects and finally rate of the film growth [16]. The on-line results will be used for macroscopic parameters adjusting what leads to growth optimization.

Design of effective monitoring system requires preliminary theoretical and experimental investigation including: determination if selected method can be used for studies of particular material, analysis of metrological problems, design of efficient optical coupling between the measurement system and the reaction chamber, selection of optical components and setting up the prototype.

2. Experimental

2.1. CVD system

The experiments were performed using the stain-less, water-cooled chamber with diameter of 160 mm. Fig. 1 presents the CVD system consisting of the pumping stage (a turbomolecular pump outfitted in a Roots and rotary

pump), microwave section, DC magnetic field section, gas flow and vacuum chamber. Microwave power (2.45 GHz) is generated by a magnetron and DC magnetic field is produced by two toroidal coils (3 kW power each), creating together conditions for Electron Cyclotrone Resonance (ECR).

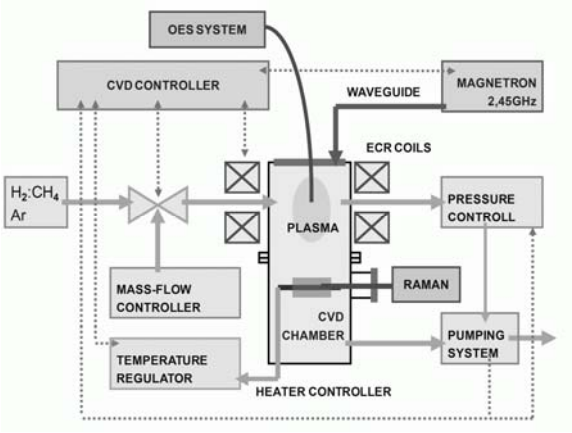


Fig. 1. Schematic diagram of experimental CVD system.

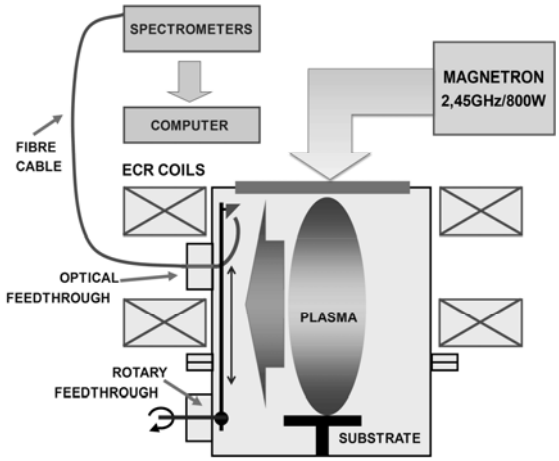
The gas mixture composition and inflow is monitored using mass flow meters and controlled by pneumatic valves. Speed of the pumping is adjusted by an angle valve to obtain constant pressure recorded with a pirani, cold cathode and baratron gauges. The pressure was stabilized to 1 Pa during the process. The molar ratio of CH_4-H_2 mixture was equal to 0.5/99.5 during investigation in accordance with previously mentioned modelling results.

2.2. Multi-point OES

A role of H_2 particles, H^+, CH_3^+ is the most important in the growth process of DLC layers. R. Manukonda has used the one-point optical emission spectroscopy as the diagnostic tool for control of plasma during the growth of diamond layers [17]. Experiments were performed using the RF CVD (Radio Frequency Chemical Vapour Deposition) plasma. Results showed that the growth of diamond layer depends strongly on the amount RF power. H. C. Barshilia and S. J. Harris carried out similar experiments [18,19]. They have studied the concentration of atomic hydrogen in methane-hydrogen plasma. We had also used the one point OES measurements in previous work [20]. These results were in accordance with other studies and molecular dynamics modelling [14,21].

Finally, those investigations were focused only on one point, averaging measurements of plasma. Such an approach is insufficient to obtain the comprehensive description of the excitation process in the ECR chamber, what considerably influences the effectiveness of the synthesis of DLC layers [22,23]. The development of the OES system for the multi-point measurements of plasma enables investigation of spatial distribution of species concentrations in plasma. Spanos et. al. describe the methods dedicated for spatial distribution monitoring of excitation [24]. This research leads to the comprehensive spatial study of plasma. However, the method is complex and time-consuming one as well as it requires the large viewport in the chamber. Moreover, the technological CVD system used in this work differs considerably from the other setups. Differences result from the process of excitation (microwave excitation in the ECR regime) and geometrical parameters of the chamber. Thus, authors of this paper proposed design the multi-point OES system dedicated for DLC synthesis systems.

The multi-point system consists of fibre-optic sensor, optical feedthrough and spectrometric detection. The concept of the OES system is presented in Fig. 2.



a)

b)

Fig. 2. Multi-point OES system: (a) - coupling with the CVD chamber, (b) prototype of optical sensor head.

The optical sensor is mounted inside the chamber on the special linear translation rail. The rail enables vertical translation of the sensor head along the longer axis of the chamber. The position of the head is shifted by the

automatic rotary motion drive via the feedthrough. The sensor consists of optical head and fibre cable supplied in metal shielding with PTFE inner tubing for higher temperature and radical atmosphere. The head of the sensor was built using parabolic off axis mirror (diameter of 25 mm and angle of 90°), which couples the optical signal into the fibre bundle with diameter core of 600 μm and numerical aperture equal to 0.37. The design enables measurements only in circular sectors of plasma emission. The spatial resolution of system is about 25 mm. The resolution of the system was optimized due to results of magnetic induction modelling in the ECR chamber (OPERA 3D software package). The position of electron resonance area was the most important parameter of the OES monitoring. The intensity level of optical signal in detection part, geometric size of the chamber (above 700 mm) and the time of single scan was also taken into consideration.

The optical signal obtained from the sensor is transmitted through the feedthrough and the fibre cable to the spectrometers. The system of spectrometers working in UV-VIS-NIR range was used for the detection of emission spectra. It is based on: three-channel spectrometer (Monolight 6800) working in the wavelength range extending from 400 to 5000 nm with spectral resolution from 1 to 5 nm and the echelle type spectrometer (Mechelle 900/ CCD KX1E) working in the wavelength range from 210 to 1100 nm with resolution of 0.3 nm. The measurement range is switched by the automated mirror system. To analysis of the spatial composition of species in plasma and the visualisation of results of scans, the dedicated software package was created.

2.3. Raman systems

One of the most important aims of presented research was to develop a dedicated Raman system with fibre-optic probes for non-invasive Raman monitoring without disturbance of the process. Preliminary *ex-situ* measurements were made using Raman microscope Jobin Yvon T6400 with Argon-ion laser. The aims of the preliminary research were as follows: studies of spatial homogeneity of film molecular composition (determination, what kind of information can be obtained from Raman studies) and getting data useful in design work of the developed Raman system (e.g. properties of investigated objects, sufficient excitation wavelength and power). Preliminary *ex-situ* measurements made for excitation wavelength extending from 472 to 514.5 nm as well as analysis of present state of art in laser technology and spectral characteristics of components of CVD and Raman systems showed that excitation wavelength λ_0 = 532 nm should be sufficient one. Spectroscopic measurements (e.g. OES presented in this paper) showed that in respective Raman range optical interfering signals originating from plasma discharge and thermal emission of substrate heater should not disable Raman *in-situ* monitoring.

The developed system for *in-situ* monitoring and control of the CVD process uses glancing-incidence configuration and has a working distance equal to 197 mm. Setup of the system and its coupling with CVD chamber is shown in Fig. 3. All components of the Raman system are placed outside the CVD chamber and remote access is provided. Optical signals are transmitted through long optical waveguides (thus protecting sensitive detection part), dedicated probes and glass windows in the chamber walls. Solid state laser Roithner DPSSL-200 (λ_0 = 532 nm, line width – 0.1 nm, output power - 200 mW, TEM_{00} transverse mode) was applied. Spectrograph Kaiser HoloSpec f/1.8i with holographic grating provides high throughput and Raman range 20-2360 cm^{-1} with spectral resolution better than 5 cm^{-1}. TE-cooled CCD detector Andor DV-401-BV ensures low level of noise.

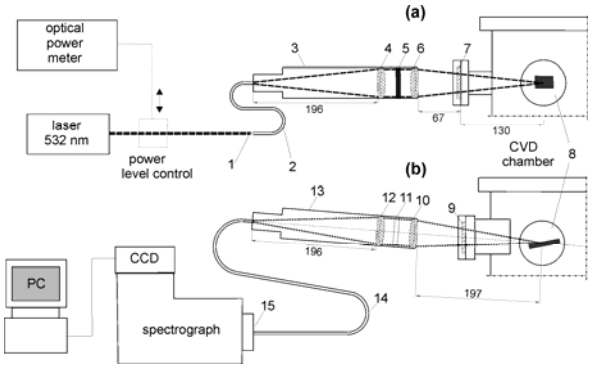


Fig. 3. Design of Raman system for monitoring of μPA CVD process: (a) excitation part, (b) acquisition part; 1- coupler, 2 - optical fibre, 3 - excitation probe, 4, 6, 10, 12 – lenses, 5 – bandpass filter, 7, 9 - windows, 8 - growing film, 11 - notch filter, 13 - collecting probe, 14 - fibre bundle, 15 - adapter; dimensions are given in millimeters.

3. Results and discussion

3.1. Plasma monitoring

The OES system was tested using H_2:CH_4 (95%:5%) mixture at flow of 25 sccm as an input gas. The preliminary experiments were performed as a function of input microwave power up to 800 W. The level of magnetic induction during the experiments was constant. The currents of ECR coils were set to 200 A. It generates the electron resonance effect in area of inductance of 87.5 mT in the chamber. The spatial position of the fibre-optic head was static in presented studies. The main purpose of this research was to test and measure the efficiency and sensitivity of species concentration monitoring.

The main optical emission lines originating from H, CH and C_2 species were recorded (see Table 1) [15]. Moreover, the atomic hydrogen line P_∞ at 820 nm was recorded, which confirms dissociation and subsequent excitation of ionization of hydrogen molecules . It corresponds to ionization and recombination of H^+, the most important species for diamond layer growth [15].

Table 1. Optical emission line observed for the mixture of H_2:CH_4.

Species	Transition	Peak position [nm]
H_α	Balmer n = 3 → n = 2	656.3
H_β	Balmer n = 4 → n = 2	486.1
H_γ	Balmer n = 5 → n = 2	434
H_δ	Balmer n = 6 → n = 2	410
H_2	$G^1\Sigma_g \rightarrow B^1\Sigma_u$	462.9
H^+	Paschen n = ∞ → n = 3	820
CH	$B^2\Delta \rightarrow X^2\Pi$	387
CH	$A^2\Delta \rightarrow X^2\Pi$	431.5
CH^+	$A^1\Pi \rightarrow X^1\Sigma$	417.1
CH^+	$A^1\Pi \rightarrow X^1\Sigma$	422.2
C_2	Swan $A^3\Pi_g \rightarrow X^3\Pi_u$	501.5
C_2	Swan $D^3\Pi_g \rightarrow A^3\Pi_u$	516.3

Fig. 4 shows the typical optical emission spectra of H_2:CH_4 mixture plasma produced with 800 W microwave power (gas flow 25 sccm). The most numerous group of the bands in the spectrum belongs to Balmer series, because of major quantity of hydrogen (95%) in the input flow mixture.

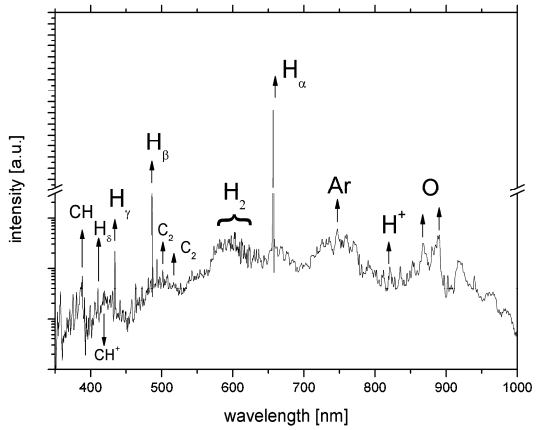


Fig. 4. Typical emission spectra of the H_2:CH_4 plasma (microwave power 800 W and gas flow 25 sccm).

The small intensities of C_2 Swan series lines concerned with CH_4 excitation and decomposition were noticed. It should be added, that the CH and CH^+ lines also appear in the emission spectra. Their intensities and the Balmer series lines could be used to measure of CH_3^+ concentration. The CH_3^+ radicals strongly increase the growth ratio of DLC layers [14], but its emission lines are placed in deep ultraviolet. This factor made the OES monitoring of this radicals as an extremely difficult and cost-consuming.

The small amount of argon and oxygen was also noticed. It is caused by residual amount of these gases in vacuum system. The argon line was recorded because experiments were carried after bell jar run-purge. The oxygen bands result from not evacuated residual gases. The argon and oxygen lines significantly decreased with longer time of pumping.

The relationship between the emission intensities of lines (H_x, P_∞, C_2, CH) and increasing microwave power was studied. The intensity ratios related to H_β were used to estimate the variation of lines intensities. The range of power was restricted to 800 W because of technical limitation. Fig. 5 shows the dependence of major hydrogen lines as a function of microwave power, which is introduced to the ECR area. The most of intensity ratios exhibits strong influence power on excitation and ionization processes.

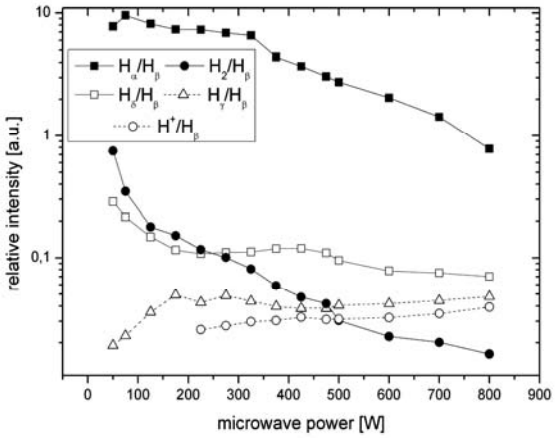


Fig. 5. Ratio of optical emission intensities of lines vs. microwave power.

The H_α/H_β and H_2/H_β ratios strongly decrease for the higher microwave power. It is result of excitation of hydrogen to the higher energy levels. This trend will be continued for the higher power levels. The intensity ratio of H_δ/H_β shows small drop and become saturated. The saturation of H_δ/H_β ratio is concerned with limited efficiency of excitation due to the insufficient level of microwave power. However, the slight increase of H_γ/H_β and H^+/H_β ratios for the higher power levels were observed. It proves that the process of excitation enables obtaining the highest level of ionization. The values of H_γ/H_β and H^+/H_β ratios are about one order of magnitude lower than the intensity ratio of H_α/H_β. It means that only about 1% of hydrogen molecules have been ionized to the H^+ level. It suggests that process should be optimized and the higher level of microwave power is necessary. It will enable excitation of the most of hydrogen's species to the P_∞ energy level corresponding to the H^+ ions.

The influence of microwave power on CH/H_β, C_2/H_β ratios of intensity was also investigated. This relationship was not obvious but the ratios slightly increase with the higher microwave power. The concentration of methane in the investigated mixture was only 5%. Additionally, the power level was limited to 800 W and it could be insufficient for the methane excitation. It lead to the low

level of emission intensities produced by CH, CH^+ and C_2 species. Moreover, they do not enable an evaluation of the unique influence of microwave power on the methane species.

The results showed that the designed prototype of the OES system enables the sensitive measurements of concentration of the species in the microwave plasma. Further, detailed studies of influence of other system parameters (i.e. spatial distribution of concentration, methane flow, composition of the mixture, process pressure) using designed system are underway.

3.2. Layer investigation

Example of the micro-Raman spectrum of microwave-plasma-CVD diamond film with respective optical microscopic image is shown in Fig. 1. Strong sharp line at 1331 cm^{-1} can be assigned to diamond (sp^3), while amorphous sp^2 carbon („G" band) is the origin of wide band at about 1608 cm^{-1} [25]. Wide-band fluorescence signal which is result of inhomogeneous structure of the CVD product can be also observed in presented spectrum.

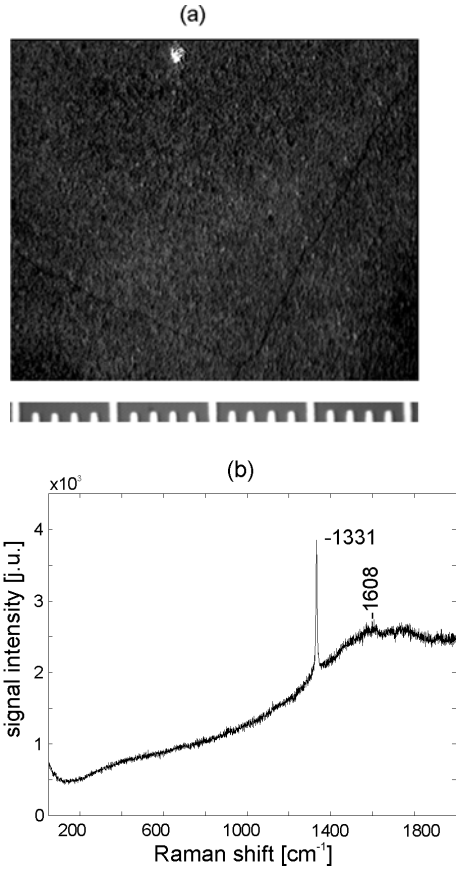


Fig. 6. Microscopic image (a) and micro-Raman spectrum (b) of microwave-plasma-CVD polycrystalline diamond film; length unit equal to 10 μm.

Ex-situ measurements confirmed that Raman measurements are powerful tool for investigation of molecular composition of diamond/DLC films. The aim of next stage was to adjust and test the dedicated Raman system for *in-situ* monitoring.

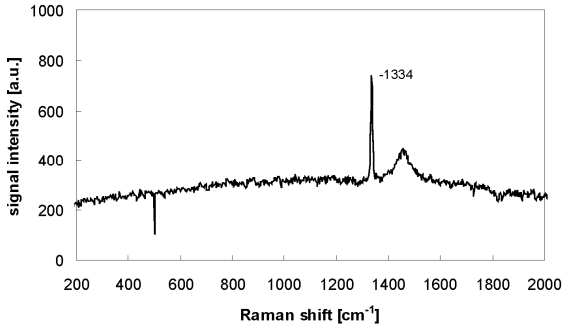


Fig. 7. Test spectrum of monocrystalline diamond recorded by the prototype of the dedicated Raman system for in-situ monitoring.

Adjustment of the prototype system at the optical plate, outside CVD chamber, enabled focusing of a beam having sufficient optical power (more than 20 mW) on the sample placed 20 cm from the excitation probe - working distance, which enables transmission of the beam through the chamber window (non-contact measurements). Sufficient efficiency of the prototype system is confirmed by test Raman spectrum presented in figure 7. Strong sharp line at 1334 cm^{-1} can be assigned to diamond (sp^3).

5. Conclusions

Research presented herein should be treated as introductory level of research work on building and adjusting of the complex optoelectronic system for CVD process monitoring. Dedicated fibre-optic setups ensure efficient optical coupling between the CVD chamber and the spectroscopic devices. Thus, multi-point OES became an effective investigation tool of the hydrogen plasma discharge as well as spatial distribution of excited atoms and molecules. Sufficient sensitivity and resolution of our OES system enabled investigation of influence of ECR macroscopic parameters such as DC current in the coils, microwave power and pumping speed on molecular composition of the plasma. Consequently, we are able to obtain atoms and ions which are the best for CVD process according to results of molecular dynamics calculations. Dedicated Raman system for in-situ monitoring of CVD processes works in glancing-incidence configuration and has working distance about 20 cm matched to the CVD chamber. Components of the measurement system (e.g. laser, filters, waveguides and lenses) were selected and their parameters were calculated. Dedicated optical waveguide probes enable safety distance between CVD chamber and sensitive components of the Raman system (e.g. CCD camera). The prototype was set up and tested. Simultaneous on-line monitoring of plasma and growing layer enable real-time optimisation of quality of the layer

(e.g. molecular composition and its homogeneity, number of defects) as well as determination of correlation between plasma composition and layer properties. Obtained results will be used in further development of the optoelectronic diagnostic system (e.g. in its modification to use with other CVD chambers). For example, modular setup of the Raman system enables simple change of excitation wavelength (e.g. to 355 nm) by replacement of laser, grating and filters.

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