Long-working-distance Raman system for monitoring the μPA ECR CVD process of thin diamond/DLC layers growth

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Abstract— The development of an optoelectronic system for Raman spectroscopic 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. A modular system for non-invasive in-situ monitoring equipped with fibre-optic probes was designed and tested. The most significant parameters of the deposited films like their molecular composition, presence of defects and rate of the film growth will be studied. Investigations with the use of optoelectronic tools will provide important data about CVD process progress as well as enable optimization of its parameters and improvement of synthesized films quality.

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

However, the average growth rate of diamond/DLC layers synthesised by PACVD (Plasma Assisted Chemical Vapour Deposition) processes is still unsatisfactory and deposited layers often contain defects and inhomogeneities of the structure. These drawbacks significantly limit the areas of their optical and microelectronic applications. Consequently, the manufacturing process requires efficient diagnostic and control tools.

The most common diagnostics of CVD manufacturing processes is based on investigating the influence of macroscopic parameters (such as microwave power, magnetic induction, gas flow and base pressure) on the layer composition and the growth rate. This approach has limited efficiency because the macroscopic process parameters can not be changed independently so their influence on the layer quality cannot be analyzed separately.

As a result, the application of in-situ monitoring of the molecular composition of a growing layer is proposed to determine what form of carbon is being deposited. The molecular composition and crystallinity determines the macroscopic properties of the layers and consequently their applications area. More amorphous layers are usually softer and smoother as well as less optically transparent [6].

Common techniques for investigation of molecular composition, e.g. X-ray diffraction and electron microscopy are time consuming and destructive for the samples. Also infrared spectroscopy can be insufficient for in-situ monitoring because of the problems with transmission of mid-IR signals between the CVD chamber and the spectroscopic system.

So Raman spectroscopy should be used in the system for in-situ monitoring of the molecular composition of the layer. Its aim would be to investigate content of carbon phases (e.g. diamond sp^3, graphite sp^2 and amorphous phases), crystallinity, content of defects and the rate of film growth [6,7].

The design of an effective monitoring system requires preliminary theoretical and experimental investigation including: determination (e.g. by preliminary measurements) if the selected method can be used for investigation of a particular material, analysis of metrological problems, design of efficient optical coupling between the measurement system and the reaction chamber (a non-invasive system requires a long working distance and efficient transmission of the measurement signals), selection of optical components as well as setting up and testing the prototype. The diamond/DLC samples manufactured in our μPA ECR CVD reactor or purchased of outside were investigated during preliminary ex-situ measurements (part of design works) and during the final tests of the prototype.

Preliminary ex-situ measurements were made using Raman microscope Jobin Yvon T6400 with Argon-ion laser (excitation wavelength extending from 472 to

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514.5 nm). The preliminary research was carried out to determine what kind of information can be obtained from the Raman studies and to get data useful in designing the Raman system (e.g. sufficient excitation wavelength and power). The spectra recorded during the preliminary investigation are shown in Fig.1 and 2.

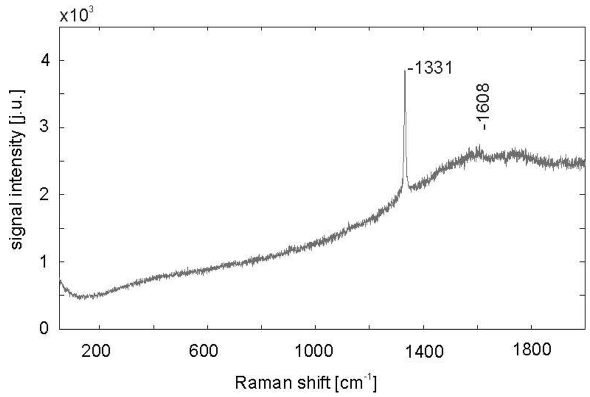

Fig. 1. Spectrum of a PA CVD diamond film; Raman microscope, excitation wavelength - 514.5 nm.

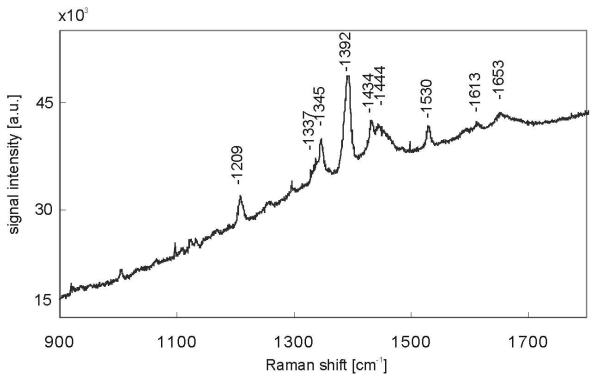

Fig. 2. Spectrum of a defected crystallite from the DLC layer deposited in our CVD chamber; Raman microscope, excitation wavelength - 514.5 nm.

The literature review [6,7] and spectra shown in Fig. 1-2 suggest that green lasers are suitable excitation sources. Bands assigned to sp^3 hybridized carbon (1331 cm^{-1} in Fig. 1 and probably 1337 cm^{-1} in Fig. 2) as well as numerous bands assigned to sp^2 hybridized carbon and C-H bonds prove that this range of excitation enable to detecti not only desired structures in deposided layers, but also their defects, which is necessary for efficient process diagnostics. It can be theoretically explained by resonant enhancement of bands assigned to sp^2 carbon for excitation by visible range lasers [6,7].

Moreover, spectroscopic measurements show that, in the respective Raman range, optical disturbing signals originating from laser induced fluorescence, plasma discharge and thermal emission of substrate heater would not disable Raman in-situ monitoring.

The optoelectronic Raman system was dedicated to monitor processes carried out in the μPA ECR CVD system shown in Fig. 3. The CVD system utilises a stainless, water-cooled chamber with a diameter of 160 mm, equipped with glass windows in the walls as well as with a pumping stage, microwave section, DC magnetic field section, optical emission spectroscopic system (OES), substrate heater and a gas flow controlling section. The microwave power (2.45 GHz) generated by a magnetron and a DC magnetic field produced by two toroidal coils (3 kW power each) create together conditions for Electron Cyclotrone Resonance. Gas mixture CH_4-H_2 (molar ratio equal to 0.5/99.5, pressure - 1 Pa) was used as a process precursor [8].

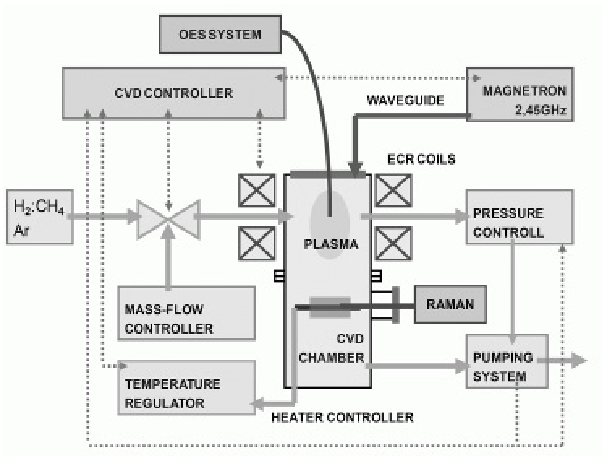

Fig. 3. Schematic diagram of the used CVD system.

The setup of the designed long-working-distance Raman system and its coupling with the CVD chamber is shown in Fig. 4.

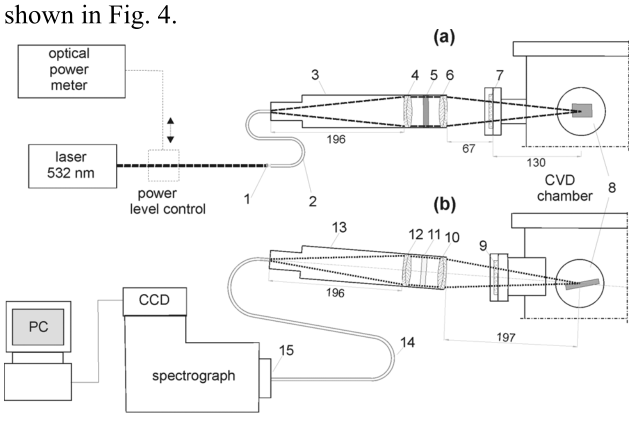

Fig. 4. Long-working-distance Raman system for monitoring of μPA CVD process: (a) excitation part, (b) acquisition part; 1- connector, 2 - optical fibre, 3 - excitation probe, 4, 6, 10, 12 – lenses, 5 – bandpass filter, 7, 9 - windows, 8 - growing film, 11 - notch filter, 13 - collecting probe, 14 -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

As a result of preliminary ex-situ measurements as well as analysis of state-of-the-art laser technology and spectral characteristics of components of the CVD system, a solid state laser Viasho DPSSL-200 (wavelength - 532 nm, line width – 0.1 nm, output power - 200 mW, TEM_{00} transverse mode) was applied as the excitation source.

Optical signals are transmitted through long optical waveguides (thus protecting the sensitive detection part), dedicated fibre-optic probes and glass windows in the chamber walls. The probes enable non-invasive process monitoring without its disturbance. They are working in a glancing-incidence configuration and have a long working distance equal to 197 mm, which enable placing all components of the Raman system outside the CVD chamber and remote access to the growing layers.

In the detection part, the spectrograph Kaiser HoloSpec f/1.8i provides high throughput and Raman range 20-2360 cm^{-1} with spectral resolution 5 cm^{-1}, while theTE-cooled CCD detector Andor DV-401-BV ensures a low level of noise.

The spectra recorded during the tests of a built long-working-distance Raman system are shown in Fig. 5 and 6. During the tests, microcrystalline diamond and PA CVD diamond films were placed inside the CVD chamber to simulate conditions similar to the CVD process monitoring

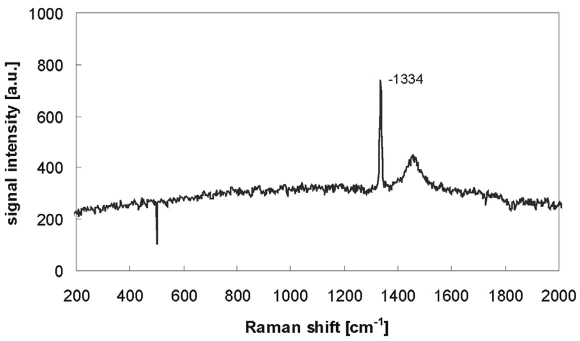

Fig. 5. Test spectrum of a monocrystalline diamond recorded by the prototype of the long-distance-working Raman system .

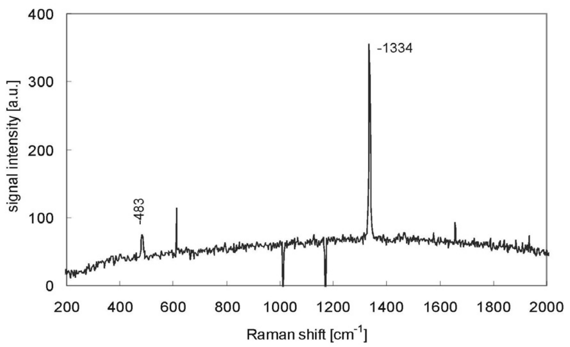

Fig. 6. Test spectrum of a thin diamond film recorded by the prototype of the long-distance-working Raman system.

The presented spectra confirm that the sensitivity of the system is sufficient even for the detection of a sp^3 diamond peak (1334 cm^{-1}), even though this peak is not enhanced by the resonance effect. The time required for a single measurement (less than 10 minutes for a thin film) is adequate for monitoring the μPA ECR CVD, which usually takes more than a few hours.

The research presented herein should be treated as an introductory level of research work on the construction and testing of an optoelectronic system for CVD process monitoring. The dedicated fibre-optic probes have the working distance of about 20 cm, well matched to the CVD chamber, thus ensuring efficient optical coupling between the CVD chamber and the spectroscopic devices as well as a safe distance between CVD chamber and sensitive components of the Raman system (e.g. CCD camera). Components of the measurement system (e.g. laser, filters, waveguides and lenses) were selected and their parameters were evaluated. The prototype was set up and tested.

The on-line monitoring of a growing layer would enable to adjust macroscopic parameters, which leads to growth optimization and determination of correlation between the CVD process parameters and layer properties.

The possibilities of further development of the designed optoelectronic diagnostic system include its modification to fit other CVD chambers. Moreover, the modular setup of the Raman system enables a simple change of the excitation wavelength (e.g. to 355 nm) by the replacement of a laser, grating and filters, which would enable resonant enhancement of a band assigned to sp^3 carbon [6,7].

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