XX IMEKO World Congress
Metrology for Green Growth
September 9−14, 2012, Busan, Republic of Korea

RAMAN DIAGNOSTICS OF CVD DIAMOND GROWTH

Marcin Gnyba

Gdansk University of Technology, Poland, marcin.gnyba@gmail.com

Abstract: Development of Raman spectroscopic system for diagnostics of growth of diamond and BDD (Boron-Doped-Diamond) thin films during μPA CVD (Microwave Plasma Assisted Chemical Vapour Deposition) process is described. Raman studies of such films were carried out as *in-situ* monitoring of film deposition as *ex-situ* measurements conducted for a sample outside the reaction vessel after manufacturing process. Modular system for the *in-situ* monitoring equipped with fibre-optic probes, was designed and tested. Moreover, Raman and optical microscopy were applied after the process for more detailed study of the deposited films. Solid state lasers having wavelength of 532 nm were applied as the excitation sources. The most significant parameters of the deposited films like their molecular composition, presence of defects and rate of the film growth were evaluated.

Keywords: Raman spectroscopy, optical measurements, in-situ monitoring, CVD, diamond layers.

1. INTRODUCTION

Thin diamond layers are promising 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) as well as because of their good chemical and electrochemical stability even in highly aggressive media and long lifetime. In doped diamond layers (e.g. boron doped diamond (BDD) these advantages are connected with better electric conductivity and a wide potential window for water discharge. These advantages enable numerous applications of the diamond and BDD films in photonics (e.g. protection coatings for the infrared optics, UV photodiodes and LEDs), microelectronics (e.g. semiconductors with the wide energy gap, FET transistors, high frequency Schottky Barrier Diodes), in environment protection (electrochemical sensors, electrodes) and in other areas (e.g. sliding layers) [1,2].

However, important for industrial application properties of devices based on the diamond and BDD films, including their lifetime and cost, are significantly determined by their manufacturing process. Moreover, average growth rate of the layers synthesised by PACVD (Plasma Assisted Chemical Vapour Deposition) processes is still unsatisfactory and deposited layers often contain defects and inhomogeneities in the structure. These drawbacks significantly limit the areas of optical and microelectronic application. Therefore, manufacturing process requires efficient diagnostic and control tools.

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

Therefore, application of an *in-situ* monitoring of molecular composition of the growing layer is proposed to determine what form of carbon is being deposited. The molecular composition and crystallinity determines macroscopic properties of the layers and thus - their applications area. In example, more amorphous layers are more softer and smoother and less optically transparent they are. 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 problems with transmission of mid-IR signals between the CVD chamber and the spectroscopic system. Thus, use of Raman spectroscopy seems to be the most promising [3,4].

2. MEASUREMENT CONCEPT

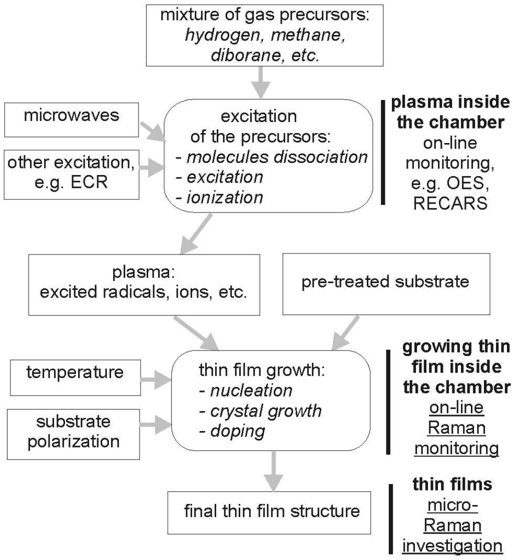

Fig. 1. Diagram showing main stages of the CVD diamond manufacturing process and assigned spectroscopic measurement methods.

The research presented in this paper refers to the films synthesised in μPA CVD (Microwave Plasma Assisted Chemical Vapour Deposition) processes. Aims and concept of use of Raman spectroscopic measurements in diagnostics of the CVD process is shown in Fig.1. It is assumed that both: progress of the CVD process and quality of the diamond layers must be investigated. In case of the CVD deposition of the diamond films and the BDD films investigation should provide data about content of carbon phases (e.g. diamond sp^3, graphite sp^2 and amorphous phases), crystallinity, content of dopants and defects as well as rate of the film growth.

Raman studies of the films can be carried out as *in-situ* monitoring of film deposition as *ex-situ* measurements conducted for a sample outside the reaction vessel after manufacturing process.

First mode gives more possibilities for control and fast on-line correction of the manufacturing process parameters. Thus, it reduces average usage of materials and energy required by the CVD technology. However, the non-invasive monitoring without process disturbance requires dedicated measurement system having efficient transmission of the measurement signals and should have long working distance (in case of the CVD chambers - 20 cm and more), which would enable placing components of the Raman system outside the chamber and remote access to the growing layers. Moreover, in practical applications number of places on the sample which can be monitored in the real time as well as spatial resolution of this measurement are limited. Thus, amount of information that can be obtained from the *in-situ* monitoring is limited.

In such circumstances, the second mode of Raman measurements – *ex-situ* Raman microscopy applied after the process - can be used as a complementary tool for more detailed study of the deposited films. Its advantages are better spatial resolution and possibility of mapping molecular composition on whole sample. However, the mapping requires long time of measurement and thus it cannot be performed efficiently in the *in-situ* mode.

One of the most significant problems in the investigation of thin films is low level of a useful Raman signal, which is result of a small sample path length and, in some cases, optical properties of investigated materials. Moreover, for some applications, especially *in-situ* monitoring, significant problem of precise excitation of selected part of investigated structure occurs. Consequently, sophisticated optical setups must be applied to ensure sufficient sensitivity of the measurement system.

3. MEASUREMENT SYSTEMS

Design of Raman system for *in-situ* measurements: Design of effective monitoring system requires preliminary theoretical and experimental investigation including: determination (e.g. by preliminary measurements) if selected method can be used for investigation of particular material, analysis of metrological problems, design of efficient optical coupling between the measurement system and the reaction chamber, selection of optical components as well as setting up and testing the prototype.

The Raman *in-situ* system presented in this paper is dedicated to monitor processes carried out in the μPA ECR CVD chambers used in our laboratory: (1) home-made MAX II ECR CVD and (2) Seki Technotron AX5200S. However, this Raman system can be refit and adapted to work with other CVD chambers equipped with windows.

The ECR CVD system MAX II utilises stain-less, water -cooled chamber with diameter of 160 mm, equipped with glass windows in the walls as well as with a pumping stage, a microwave section, a DC magnetic field section optical emission spectroscopic system (OES), substrate heater and a gas flow controlling section. Microwaves (2.45 GHz, power up to 5 kW) generated by a magnetron and 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 is used as a process precursor. The AX5200S system similar construction of the chamber, the main difference is lack of the ECR setup and lower level of microwave power (up to 1.5 kW).

Setup of designed long-working-distance Raman system and its coupling with the CVD chamber is shown in Fig. 2. The measurement system utilizes a modular setup equipped with dedicated fibre-optic probes having working distance of appox. 20 cm. Optical signals are transmitted through long optical waveguides, the probes and glass windows in the CVD chamber walls. All components of the Raman system are placed outside the chamber and remote access to the growing layers is provided.

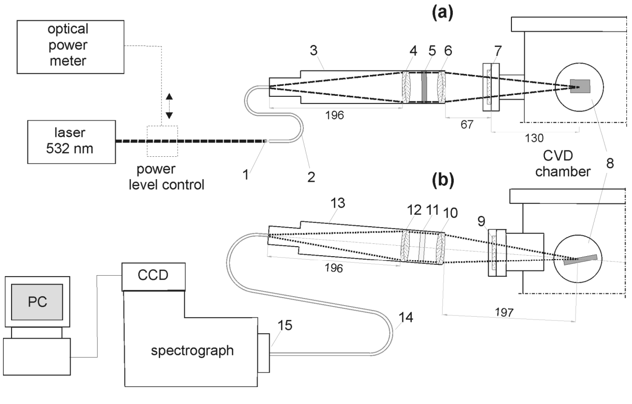

Fig. 2. Long-working-distance Raman system for monitoring of μPA CVD process: (a) excitation part, (b) acquisition part; 1- coupler, 2 - optical fibre, 3 - excitation probe, 4, 6, 10, 12 – lenses, 5 – bandpass filter, 7, 9 - windows, 8 - growing film, 11 - notch filter, 13 - collecting probe, 14 - fibre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

As a result of preliminary *ex-situ* measurements and analysis of spectral characteristics of components of the CVD system, solid state laser Viasho DPSSL-200 (wavelength - 532 nm, line width – 0.1 nm, output power - 200 mW) was applied as the excitation source. Optical signals are transmitted through long optical waveguides (thus protecting sensitive detection part), dedicated fibre-optic probes and glass windows in the chamber walls. The probes are working in glancing-incidence configuration [4]. In detection part, spectrograph Kaiser HoloSpec f/1.8i provides high throughput and spectral resolution 5 cm^{-1} within Raman range 150-2360 cm^{-1}, while TE-cooled CCD detector Andor DV-401-BV ensures low level of noise.

Sodium spectral lamp is being used for wavelength calibration.

Raman microscope: More detailed investigation of molecular composition of the films and its homogeneity was carried out *ex-situ* for samples removed from the CVD chamber by means of Raman spectroscopy. A HORIBA LabRAM ARAMIS Raman confocal microscope (100x/0.95 objective, 50 µm of confocal aperture) equipped with a 532 nm DPSS laser was used. Three measurement procedures were applied: (1) single point measurement, (2) preliminary investigation of the surface of the film by optical microscopy and subsequent Raman measurement in selected places, (3) Raman mapping of selected area of the film.

4. RESULTS OF MEASUREMENTS

Tests of systems of the Raman for on-line measurements: The Raman system for *in-situ* monitoring was used to record spectra of PA CVD diamond films placed inside the CVD MAX II system. Spectrum of the diamond film deposited on quartz substrate is shown in Fig. 3.

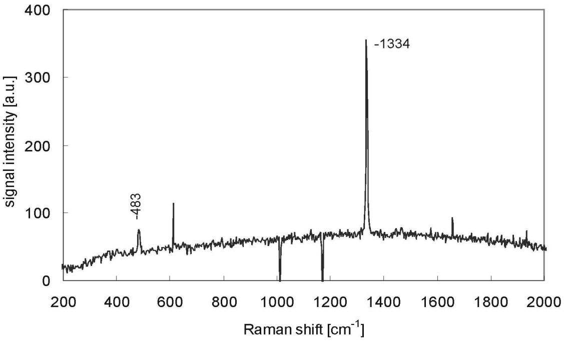

Fig. 3. Test spectrum of thin diamond film deposited on quartz substrate recorded by the prototype of the long-distance-working Raman system.

Presented spectrum confirms that sensitivity of the system is sufficient for detection of sp^3 diamond peak (observed for Raman shift value - 1334 cm^{-1}) [5-7], even though this peak is not enhanced by a Raman resonance effect. Required time required for single measurement (less than 10 minutes for thin film) is adequate for monitoring of the µPA ECR CVD, which usually take more than a few hours. Moreover, the glancing incidence optical configuration enables reduction of interfering signals originating from the substrate (band at 483 cm^{-1} – quartz) [5-7].

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

Raman microscopic investigations: Use of Raman microscopy after deposition provides more detailed information about homogeneity and molecular composition of the layer. Raman microscopic spectrum of the diamond microcrystalline film is shown show in Fig. 4. The optical microscopic image suggests that the film contains defects – is not homogeneous. Peaks at 1332 cm^{-1} assigned to diamond sp^3 phase are observed in both spectra. However, in curve B also bands assigned to unwanted chemical bonds: wide band at 1549 cm^{-1} assigned to amorphous sp^2 carbon („G" band) and band at 2832 cm^{-1} assigned to C-H stretching can be observed. In spectrum of CVD thin film we can also observe stronger wide-band fluorescence signal, which is result of inhomogeneous structure of the CVD product. It confirms that there is a chemical point defect of the film in place marked B at the picture (Fig. 4). A peak at 520 cm^{-1} is assigned to the silicon substrate [5-7].

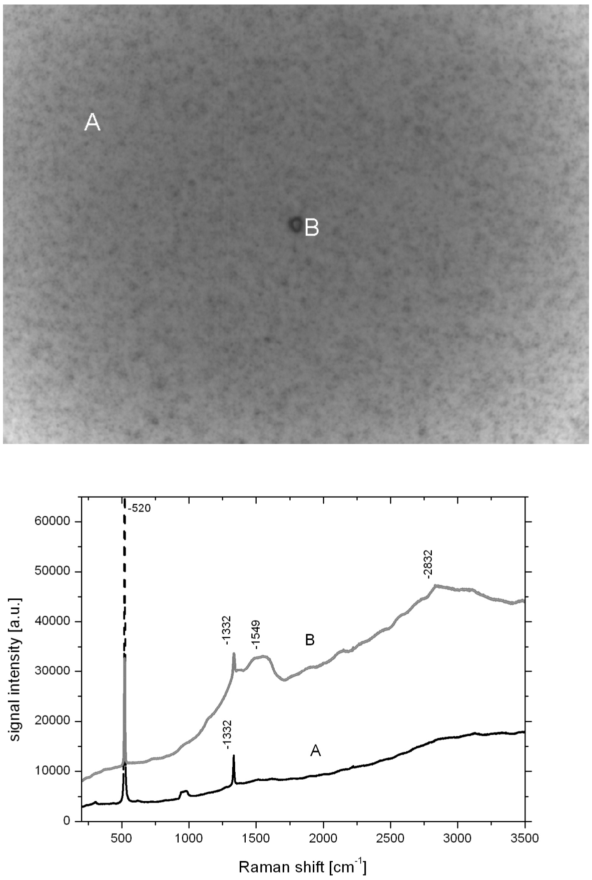

Fig. 4. Optical microscopic image of diamond thin film and Raman spectra collected in places marked at the picture.

Microscopic spectra of the BDD films having low and high concentration of boron are presented in Fig. 5. It is clearly noticeable that both spectra share common features, typical for the boron-doped diamond layers. One of them is a broad Raman signal centered at 483 cm $^{-1}$, while the other is centered at 1204 cm^{-1} (for low B content) and 1216 cm^{-1} for (higher B content). Hypothesizes about origins of these bands include phonon scattering at boron-induced structural modifications, electronic transitions involving boron, or scattering at acoustic and optical phonons activated by defects in the lattice [8-13]. along with a sharp Raman peak at 1315 cm $^{-1}$. The diamond sp^3 phonon peak at 1332 cm^{-1} is shifted towards lower wavenumbers (1315 cm^{-1} at the black curve) for higher content of born dopant, which refers to distortion of the diamond lattice. Moreover, shape of the peak is asymmetrical. This is ascribed to the Fano effect, the interaction between discrete phonon and continuum of electronic levels of the same energy [8-13]. Thus, it can be concluded that position and intensity of these three Raman bands can be used to measure content of the boron dopant in the BDD films.

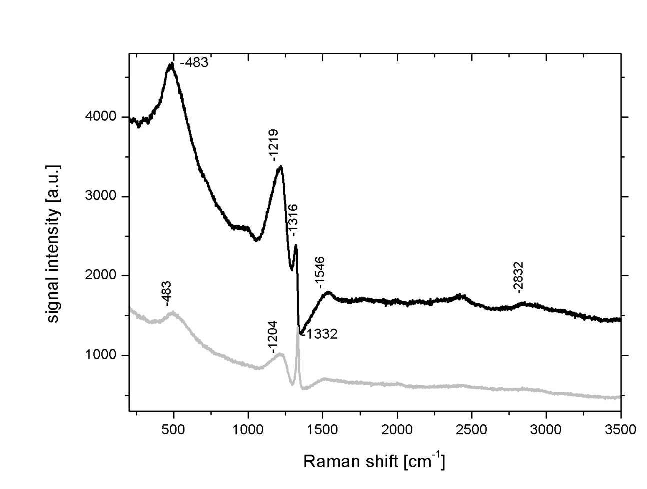

Fig.5. Micro-Raman spectra of the BDD layers: black curve- high concentration of the dopant, grey curve – low concentration of the dopant.

A weak wide band at 1546 cm^{-1} assigned to a "G-band" of the sp^2 amorphous carbon and a weak wide band at 2832 assigned to C-H stretching proves presence of structures other than diamond lattice distorted by boron (probably mainly surface defects).

5. CONCLUSIONS

Development of the optoelectronic system for non-invasive monitoring of diamond thin films growth during µPA CVD process is described. The most significant parameters of the deposited film like molecular composition of the film (content of diamond sp^3 and amorphous phases), presence of defects and rate of the film growth can be investigated by means of Raman spectroscopy. Results of optoelectronic investigation enable improvement of CVD process parameters and synthesized DLC films quality.

Research presented herein should be treated as introductory level of research work on building and adjusting of the optoelectronic system for CVD process monitoring. Dedicated fibre-optic probes have working distance about 20 cm matched to the CVD chamber thus ensuring efficient optical coupling between the CVD chamber and the spectroscopic devices as well as 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 calculated. The prototype was set up and tested.

On-line monitoring of growing layer would enable macroscopic parameters adjusting what leads to growth optimization and determination of correlation between process parameters and layer properties.

A possibility of further development of designed optoelectronic diagnostic system includes its modification to use with other CVD chambers. Moreover, modular setup of the Raman system enables simple change of excitation wavelength (e.g. to 355 nm) by replacement of laser, grating and filters.

6. ACKNOWLEDGEMENTS

The research was carried out in frame of the NCN project no. 5106/B/T02/2011/40, the multi-year programme project no. PW-004/ITE/03/2005, by the NCBiR project LIDER/20/91/L-2/10 and scientific activity of the Faculty of Electronics, Telecommunication and Informatics of GUT.

7. REFERENCES

[1] P.W.May, Diamond thin films: a 21st-century material. Phil. Trans. R. Soc. Lond. A. Vol. 358, pp. 473-495, 2000.

[2] R.F. Davis, Diamond Films and Coatings. Development, Properties and Applications, Noyes Publications, Park Ridge, 1993.

[3] M. Pelletier, Analytical Applications of a Raman Spectroscopy, Blackwell Science, Oxford, 1999.

[4] H.J. Bowley, D.J. Gardiner, D.L. Gerrard, P.R. Graves, J.D. Louden, G. Turrel, Practical Raman Spectroscopy. Springer Verlag, Berlin, 1991

[5] M. Rudigier and R. Haubner, "Characterisation of diamond coatings with different morphologies by Raman spectroscopy using various laser wavelengths", Analytical and Bioanalytical Chemistry, vol./is. 403/3(675-81), 1618-2650, May 2012.

[6] M. Kahn and W. Waldhauser, "Raman Spectroscopy of Carbon Based Films – Spectra Interpretation and Selected Applications", BHM Berg- Und Hüttenmännische Monatshefte, Vol. 155, Iss. 11, pp. 534-540, November 2010.

[7] D. Lin-Vien, N. Colthrup, W. Fateley, J. Grasselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press Inc., San Diego, 1991.

[8] P. Wurzinger, P. Pongratz, P. Hartmann, R. Haubner, and B. Lux, "Investigation of the boron incorporation in polycrystalline CVD diamond films by TEM, EELS and Raman spectroscopy", Diamond and Related Materials Vol. 6, Issues 5–7, pp. 763–768, April 1997.

[9] P. C. Ricci, A. Anedda, C. M. Carbonaro, F. Clemente, and R. Corpino, "Electrochemically induced surface modifications in boron-doped diamond films: a Raman spectroscopy study", Thin Solid Films vol. 482, pp.311-317, June 2005.

[10] [11] M. Mermoux, F. Jomard, C. Tavarès, F. Omnès, and E. Bustarret, "Raman characterization of boron-doped {111} homoepitaxial diamond layers", Diamond and Related Materials, Vol. 15, Iss. 4–8, pp. 572–576, April–August 2006

[11] A. Crisci, M. Mermoux, and B. Saubat-Marcus, "Deep ultra-violet Raman imaging of CVD boron-doped and non-doped diamond films", Vol. 17, Iss. 7–10, pp. 1207–1211, July–October 2008

[12] F. Pruvost, E. Bustarret, and A. Deneuville, "Characteristics of homoepitaxial heavily boron-doped diamond films from their Raman spectra", Diamond and Related Materials, Vol. 9, Iss. 3–6, pp. 295–299, April–May 2000.

[13] M. Bernard, A. Deneuville, and P. Muret, "Non-destructive determination of the boron concentration of heavily doped metallic diamond thin films from Raman spectroscopy", Diamond and Related Materials Vol. 13, Iss. 2, , pp. 282–286, February 2004.