DOI: 10.2478/v10077-009-0015-z

P. Wroczyński, R. Bogdanowicz, M. Gnyba
Gdansk University of Technology, Faculty of Electronics, Telecommunication and Informatics, Department of Optoelectronics and Electronic Systems, Gdansk, Poland

OPTOELECTRONIC SYSTEM FOR INVESTIGATION OF CVD DIAMOND/DLC LAYERS GROWTH

ABSTRACT

Development of the optoelectronic system for non-invasive 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 system uses multi-point Optical Emission Spectroscopy (OES) and long-working-distance Raman spectroscopy. Dissociation of H_2 molecules, excitation and ionization of hydrogen atoms as well as spatial distribution of the molecules are subjects of the OES investigation. The most significant parameters of the deposited film like molecular composition of the film can be investigated by means of Raman spectroscopy. Results of optoelectronic investigation will enable improvement of CVD process parameters and synthesized DLC films quality.

Key words: *CVD, diamond/diamond-like-carbon layers, optical emission spectroscopy, Raman spectroscopy*

INTRODUCTION

Diamond and DLC (Diamond-Like-Carbon) thin layers are promising materials for optoelectronics and microelectronics because of their extraordinary properties, e.g. high hardness, low dielectric constant, wide energy band gap, high resistivity, wide spectral range of optical transmission and high thermal conductivity [1]. However, the growth rate of the high quality films synthesised by PA CVD (Plasma Assisted Chemical Vapour Deposition) processes is still unsatisfactory (~1 μm/h) [2,3]. Moreover, the layers are not homogeneous, but they are compositions of sp^3 diamond phase mixed with various sp^2 and amorphous fragments. Therefore, although some parameters of these layers approaches parameters of diamond, there are not the same. These factors significantly limit the applications area of the films. [4]
Manufacturing of high quality thin films requires effective diagnostics of the low-pressure plasma process. The most of the studies of diamond/DLC manufacturing processes are based on macroscopic parameters measurement, e.g. microwave power, magnetic induction, gas flow and base pressure as well as on analysis of their influence on the layer composition and the growth rate. This approach is inadequate, because the macroscopic parameters can not be changed independently, so their influence on the layer quality can not be analyzed separately. In this study the novel molecular approach is used. The aim of presented research was to develop a system for in-situ monitoring of

molecular-level reactions taking place during the films growth. Design of the monitoring system requires preliminary research including: selection of a methods an their theoretical analysis, design of an efficient coupling between the measurement system and the reaction chamber as well as setting up a prototype.
A few scientific papers present discussion about role of particular particles (radical, ion) in reaction of carbon atoms on the growth surface. Results of analyses and molecular dynamics modelling of low-pressure growth of diamond/DLC films presented there suggest 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 [5]. To check this predictions experimentally, authors decided to build the optoelectronic system for simultaneous investigation of the CVD plasma excitation and the layer growth. A Spatially Resolved Optical Emission Spectroscopy (SR-OES) was selected to investigate distribution of excited particles in the plasma, while Raman spectroscopy - to study molecular composition of the layers. Developed spectroscopic system is dedicated to μPA ECR CVD (Microwave Plasma Assisted Electron Cyclotron Resonance CVD) system. The concept and aims of the investigation are shown in Fig.1.

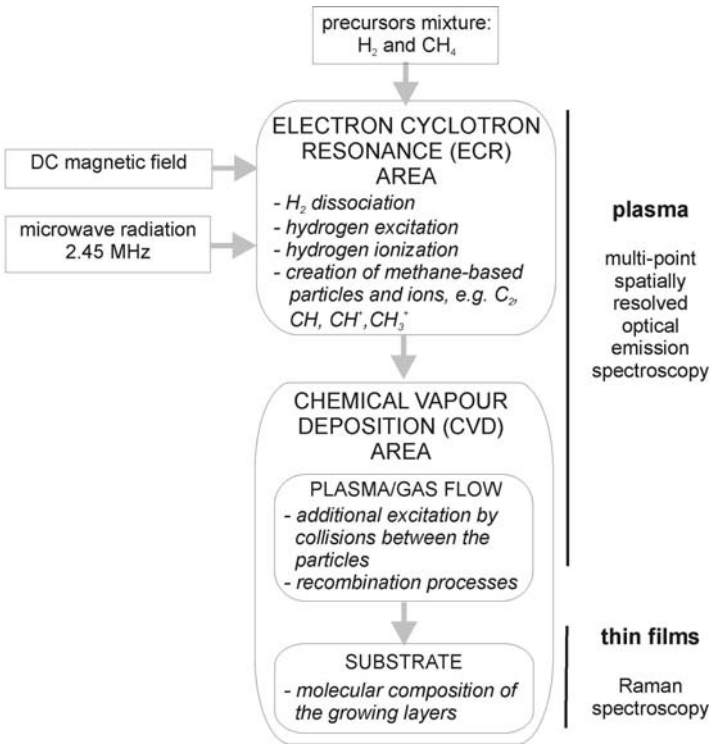

Fig. 1. Concept diagram of spectroscopic investigation of PA ECR CVD process of diamond/DLC film deposition; Italic-style text refers to detailed aims of the investigation

EXPERIMENTAL

CVD system

The used μPA ECR CVD system consists of a stain-less steel, water-cooled vacuum chamber (diameter equal to 160 mm) with a pumping stage (a turbomolecular pump

outfitted in a Roots and rotary pump), a microwave section, a DC magnetic field section and a gas flow controller [6,7]. Mixture of CH_4 and H_2 (molar ratio equal to 0.5/99.5%) is used as a precursor. Total gas flow is up to 100 sccm, while range of its total pressure extends from 0.1 to 10 Pa. 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. Plasma is generated in area of Electron Cyclotron Resonance between microwave radiation (2.45GHz, power up to 3 kW) and DC magnetic field (induction - 87.5 mTesla) from two toroidal coils.

Multi-point SR-OES system

Most of already presented papers on investigation of hydrogen-methane-based CVD plasma referred to single-point, averaging OES measurements [8]. Such an approach is insufficient to obtain the comprehensive description of the excitation process in the ECR area [9]. Therefore, we designed the multi-point SR-OES system (Fig. 2). This system consists of fibre-optic sensor, optical feedthrough and spectrometric detection. The sensor, consisting of optical head and fibre cable, is mounted inside the chamber on the special linear translation rail, which enables vertical translation of the sensor head 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 a fibre bundle. Then, the signal is transmitted to the spectrometers working in UV-VIS-NIR range: three-channel spectrometer Monolight 6800 working in range from 400 to 5000 nm with resolution 1 - 5 nm and Mechelle 900 (with CCD KX1E) spectrometer working in range from 210 to 1100 nm with resolution of 0.3 nm.

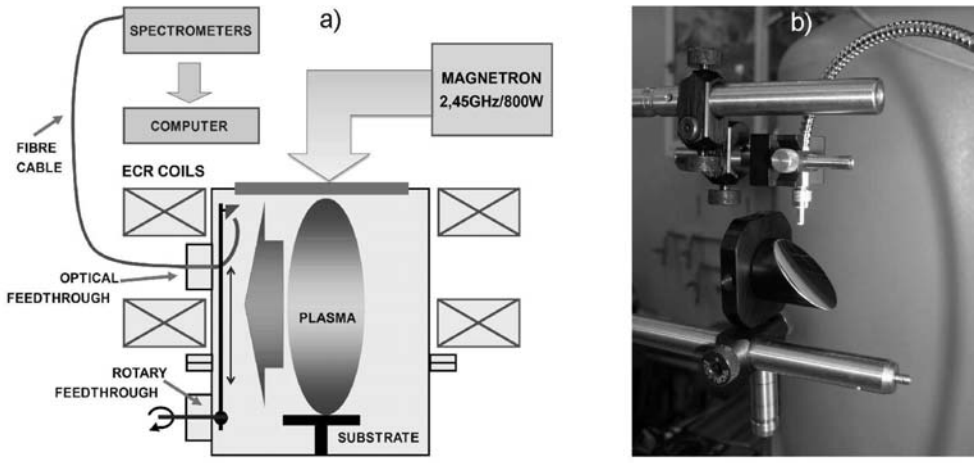

Fig. 2. Multi-point SR-OES system: (a) - coupling with the CVD chamber, (b) prototype of optical sensor head

Raman system

Raman system with fibre-optic probes for non-invasive monitoring is shown in Fig. 3.

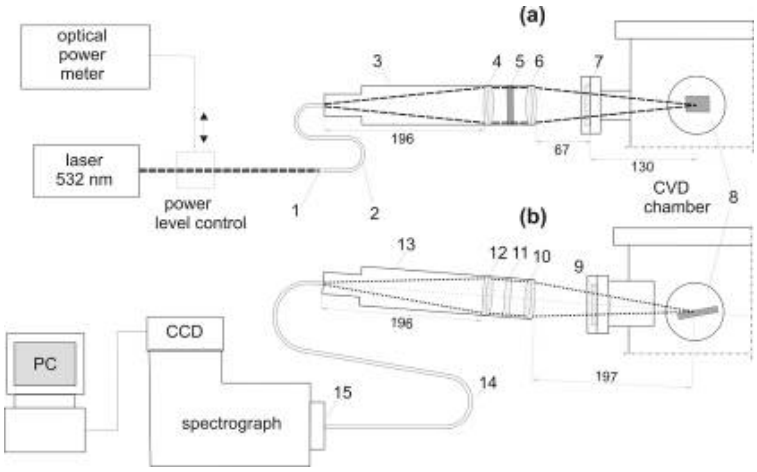

Fig. 3. Design of Raman system for monitoring of PA CVD process: (a) excitation part, (b) acquisition part; 1- coupler, 2 - optical fibre, 3 - excitation probe, 4, 6, 10, 12 – lenses, 5 – bandpass filter, 7, 9 - windows, 8 - growing film, 11 - notch filter, 13 - collecting probe, 14 - fibre bundle, 15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

Preliminary *ex-situ* measurements and theoretical analysis showed that excitation wavelength 532 nm should be sufficient. Spectroscopic measurements (e.g. OES) showed that plasma and substrate heater optical emissions should not interfere Raman monitoring [7,10]. The Raman system uses glancing-incidence configuration optics having a working distance equal to 197 mm. Components of the Raman system are placed outside the CVD chamber. Optical signals are transmitted through long optical waveguides (thus protecting sensitive detection part), dedicated probes and glass windows in the chamber walls. DPSSL laser (532 nm, 200 mW, line width – 0.1 nm), Kaiser HoloSpec f/1.8i spectrograph, CCD detector Andor DV-401-BV were applied, providing Raman range 20-2360 cm^{-1} with resolution 5 cm^{-1}.

RESULTS AND DISCUSSION

OES plasma monitoring

Sensitivity of the system was tested. Example of the recorded spectrum is shown in Fig. 4.

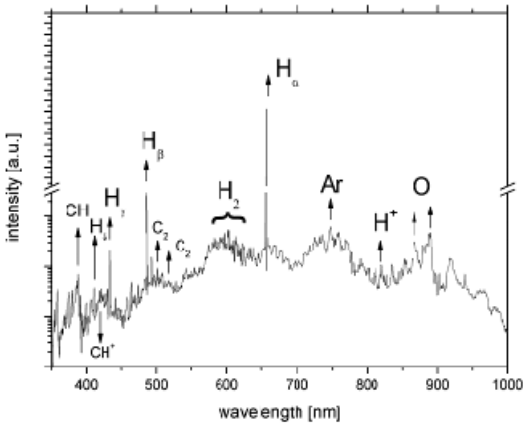

Fig. 4. Typical emission spectra of the H_2:CH_4 plasma (microwave power 800 W and gas flow 25 sccm)

Following emission lines originating from exited hydrogen and hydrocarbonate species were recorded: 656.3 nm (H_α: Balmer n = 3 → n = 2), 486.1 nm (H_β: Balmer n = 4 → n = 2), 434 nm (H_γ: Balmer n = 5 → n = 2), 410 nm (H_δ: Balmer n = 6 → n = 2), 462.9 nm (H_2: $G^1 \Sigma_g \rightarrow B^1 \Sigma_u$), 820 nm ($H^+$: Paschen n = ∞ → n = 3), 387 nm (CH: $B^2 \Delta \rightarrow X^2 \Pi$), 431.5 nm (CH: $A^2 \Delta \rightarrow X^2 \Pi$), 417.1 nm ($CH^+$), 422.2 nm ($CH^+$), 501.5 nm ($C_2$: Swan $A^3 \Pi_g \rightarrow X^3 \Pi_u$), 516.3 nm ($C_2$: Swan $D^3 \Pi_g \rightarrow A^3 \Pi_u$) [11].
The atomic hydrogen line at 820 nm confirms dissociation of H_2 and creation of H^+ ions - the most important species for diamond layer growth [5,12]. Although CH_3^+ emission lines are placed in deep ultraviolet, intensity of lines assigned to C_2, CH and CH^+ can be used to estimate CH_3^+ content. The subsequent measurements showed that the designed SR-OES system has sufficient sensitivity to detect change of emission bands intensity (up to saturation) caused by change of microwave power and DC current in the coils in ranges typical to CVD process. Moreover, multi-point measurement showed decrease of ion concentration outside the ECR area caused by recombination processes.
The small detected amount of argon and oxygen is caused by residual amount of these gases in vacuum system and can be used to control efficiency of the pumping system.

Tests of the system for Raman monitoring

Sufficient efficiency of the system for Raman monitoring is confirmed by test spectrum presented in Fig. 5. Strong line at 1334 cm^{-1} is assigned to diamond, while band at 483 cm^{-1} – to quartz substrate [13]. Detection of the band assigned to sp^3 phase confirms sufficient sensitivity of developed system, because bands assigned to sp^2 carbon phases are usually strong for excitation wavelength 532 nm because of their Raman resonance enhancement [14,15].

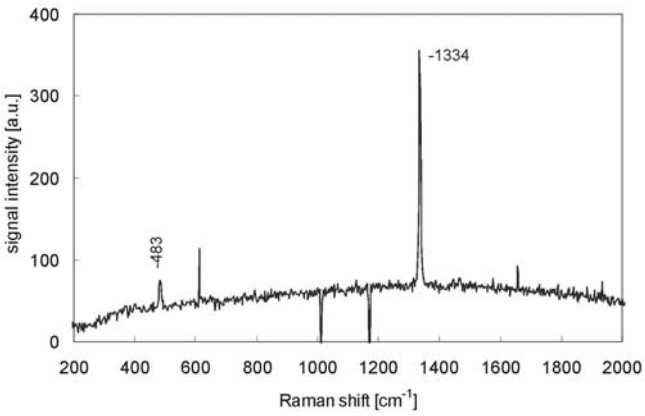

Fig. 5. Test spectrum of mPA CVD diamond layer recorded by the Raman system for *in-situ* monitoring

CONCLUSIONS

Research presented herein should be treated as introductory level of research work on building 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 SR-OES became an effective investigation tool

of the hydrogen-methane plasma discharge and spatial distribution of excited particles as a function of ECR macroscopic parameters. Thus, we are able to obtain are the best particles for CVD process. Dedicated long-working-distance Raman system enables investigation of growing layers. Further, simultaneous on-line monitoring of plasma and growing layer should enable real-time optimisation of quality of the layer as well as determination of correlation between plasma composition and layer properties.

ACKNOWLEDGMENTS

The research was carried out in frame of the multi-year programme project no. PW-004/ITE/03/2005 and funds of Faculty of Electronics, Telecommunications and Informatics of Technical University of Technology.

REFERENCES

1. May P.W., Tsai H.Y., Wang W., Smith J.A.: Deposition of CVD Diamond onto GaN, Diam. Rel. Mat. 15(4-8) (2006) pp. 526-530.
2. Hsiao-Kuo C., Sung J. C.: The rapid growth of thin transparent films of diamond, Diam. Rel. Mat. 10 (2001) pp. 1584.
3. May P.W.: The New Diamond Age?, Science 319 (2008) pp. 490.
4. Smietana M., Szmitdt J., Korwin-Pawlowski M.L., Bock W.J.: Diamond-like carbon films deposited onto optical fibres and waveguides: application in chemical sensing, Proc. SPIE 6189 (2006) pp. 186-195.
5. Herman A., Wroczynski P.: Microwave plasma assisted chemical vapour deposition for thin diamond film synthesis, Adv. Sci. and Technol. 6 (1995) pp. 141.
6. Bogdanowicz R., Gnyba M., Wroczynski P.: Optoelectronic monitoring of plasma discharge optimized for thin diamond film synthesis, J. Phys. IV 137 (2006) pp. 137 57.
7. Gnyba M., Bogdanowicz R.: Design and simulation of excitation laser system for in-situ Raman monitoring, Europ. Phys. J. ST 144 (2007) pp. 209-214.
8. Chen P.H., Lin C.L., Liu Y.K., Chung T.Y., Cheng-Yi L.: Diamond Heat Spreader Layer for High-Power Thin-GaN Light-Emitting Diodes, IEEE Phot. Technol. Lett. 20 (2008) pp. 845-847.
9. Zuo S, Yaran M., Grotjohn T.: Investigation of diamond deposition uniformity and quality for freestanding film and substrate applications, Diam. Rel. Mat. 17(3) (2008) pp.300-305.
10. Bogdanowicz R.: Investigation of H_2:CH_4 plasma composition by means of spatially resolved optical spectroscopy, Acta Phys. Pol. A. 114 (2008) pp.6-A.

11. Sobelman I.: Atomic Spectra and Radiative Transitions, Berlin, Springer-Verlag, 1992.
12. Asmussen J., Reinhard D., Dandy D.S.: Diamond Thin Films Handbook, New York, Marcel Dekker Inc., 2002.
13. Fabisiak K.: Analiza defektow w cienkich polikrystalicznych warstwach diamentowych otrzymywanych metodami CVD, Torun, Wydawnictwo UMK, 1994.
14. Mermoux M., Marcus B., Abello L., Rosman N., Lucazeau G.: In situ Raman monitoring of the growth of CVD diamond films, J. Raman Spectroscopy 34(7-8) (2003) pp.505-514.
15. Bogus A., Gebeshubera I.C., Pauschitz A., Manish R., Haubner R.: Micro- and nanomechanical properties of diamond film with various surface morphologies, Diam. Rel. Mat. 17(12) (2008) pp. 1998-2004.