Growth and characterization of nanodiamond layers prepared using the plasma-enhanced linear antennas microwave CVD system

Frantisek Fendrych, Andrew Taylor, Ladislav Peksa, Irena Kratochvilova, Jan Vlcek, Vladimira Rezacova, Vaclav Petrak, Zdenek Kluiber, Ladislav Fekete, Michael Liehr, et al.

Growth and characterization of nanodiamond layers prepared using plasma enhanced linear antennas microwave CVD system

Frantisek Fendrych[1], Andrew Taylor[1], Ladislav Peksa[1], Irena Kratochvilova[1], Jan Vlcek[2], Vladimira Rezacova[3], Vaclav Petrak[3], Zdenek Kluiber[1,3], Ladislav Fekete[1], Michael Liehr[4] and Milos Nesladek[5]

[1] Institute of Physics, Academy of Sciences of the Czech Republic, v.v.i, Na Slovance 2, CZ-18221 Prague 8, Czech Republic
[2] Department of Physics and Measurement, Institute of Chemical Technology Prague, Technicka 5, CZ-16628 Prague 6, Czech Republic
[3] Faculty of Biomedical Engineering, Czech Technical University, Sitna 3105, CZ-27201 Kladno 2, Czech Republic
[4] Leybold Optics Dresden GmbH, Zur Wetterwarte 50, D-01109 Dresden, Germany
[5] IMOMEC division, IMEC, Institute for Materials Research, University Hasselt, Wetenschapspark 1, B-3590 Diepenbeek, Belgium

Corresponding author e-mail: fendrych@fzu.cz

Abstract. Industrial applications of PE CVD diamond grown on large area substrates, 3D shapes, at low substrate temperatures and on standard engineering substrate materials require novel plasma concepts. Based on the pioneering work of the group at AIST in Japan, high-density coaxial delivery type of plasmas have been explored [1]. However, an important challenge is to obtain commercially interesting growth rates at very low substrate temperatures. In the presented work we introduce the concept of novel linear antenna sources, designed at Leybold Optics Dresden, using high-frequency pulsed MW discharge with a high plasma densitiy. This type of pulse discharges lead to the preparation of nanocrystalline diamond thin films, compared to ultra-nanocrystalline diamond thin films prepared in Ref [1]. We present OES data for the CH_4 – CO_2 - H_2 gas chemistry and we discuss the basic properties of the nanocrystalline diamond (NCD) films grown.
Keywords. nanodiamond, thin films, PE MW CVD, linear antennas
PACS. 81.05.uj, 81.07.Bc, 81.15.Gh
Submitted to J Phys D Applied Physics

1. INTRODUCTION

In recent years diamond has become a widely investigated material [1]. Ultrananocrystalline diamond (UNCD) and nanocrystalline (NCD) diamond films have attracted more and more interest due to their unique electrical, optical and mechanical properties, which make them widely suitable for different applications, such as: MEMS devices, lateral field emission diodes, biosensors, thermoelectrics, etc. Additionally nanodiamond offer properties such as biocompatibility and non-toxicity.

Typical conditions for microwave plasma assisted growth of diamond films are a mixture of a hydrocarbon and hydrogen with a very low proportion of hydrocarbon and a substrate temperature of about 600-1000ºC [2, 3, 4]. From the point of view of the material structure and properties, it is important to develop a wide range of technologies allowing growth of thin films from ultra nanocrystalline diamond – UNCD – (i.e continuously renucleating) to nanocrystalline diamond – NCD – (columnar) type of diamond growth [5]. High substrate temperatures restrict the range of suitable

substrates and therefore possible applications of these films. Another restriction of microwave plasma assisted growth is the growth area; typically it is restricted to a maximum diameter of 15cm. Again this not only restricts the range of applications but also their scale. The ability to produce diamond films at low temperatures and on large areas has been previously described [1]. The presented apparatus further extends the previously described apparatus with the addition of tunable pulsed modes.

2. EXPERIMENTAL DETAILS

2.1. Description of growth apparatus

For the growth of NCD films an original non-commercial Plasma Enhanced (PE) Linear Antenna (LA) MW (microwave) CVD apparatus is used (see Figure 1, Scheme and photo of the non-commercial Microwave Plasma Enhanced Linear Antennas Chemical Vapour Deposition apparatus). The PELAMWCVD apparatus consists of a rotary pump (producing a base pressure of 0.005 mbar - a turbomolecular pump allowing a vacuum of 10^{-7} mbar is planned), a growth chamber, a pressure control system, a process gas delivery control system, a microwave power controller and delivery system, a water cooling system and an air cooling system. The substrate temperature is measured by a Williamson Pro 92-38 infrared thermometer.

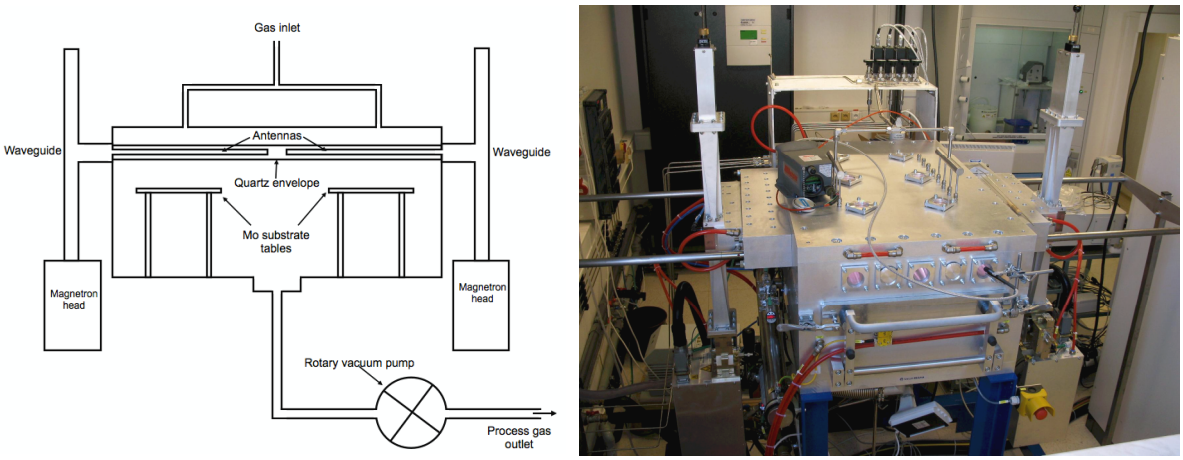

Figure 1, Scheme and photo of the non-commercial Microwave Plasma Enhanced Linear Antennas Chemical Vapour Deposition apparatus

The PELAMWCVD apparatus is capable of producing both continuous wave (at a maximum of 2 x 3 kW) and tunable pulsed microwaves (at a maximum of 2 x 10 kW). The growth chamber potentially allows the deposition on substrates up to the size of 500mm x 300mm.

Microwave power is controlled by the use of a pulse-generator, magnetron heads, rectangular tunable wave guides and coaxial power distributors. Significantly higher powers (2 x 20 kW CW) are possible by this construction due to extreme low losses. Microwaves are delivered into the growth chamber in a linear form by four pairs of antennas enclosed in quartz envelopes. The linear microwave plasma sources are arranged parallel to one another above the substrate holder (see Figure 2).

Figure 2, Microwave plasma sources arranged parallel to one another

2.2. NCD film growth conditions

Several NCD films have been produced using the following typical process conditions: Gas mixtures – H_2 (6.0 purity), CH_4 (5.5 purity) and CO_2 (5.3 purity) with various ratios, process pressure range – 0.5 mBar to 2 mBar, microwave power – up to 10.0 kW pulsed and growth time of up to 8 hours. Substrates are mounted on a molybdenum holder. The average substrate temperature during growth was measured to be 463°C. Typical substrates used are silicon, quartz and stainless steel. Substrate sizes range from 1cm^2 to 6 inch diameter wafers. Substrates were seeded with NanoAmando nanodiamond from NanoCarbon Research Institute Ltd using a methodology to reduce clusters and maximize coverage. Results reported below are from layers grown on 2 x 2cm Si substrates arranged in a 20cm diameter array with the same growth conditions unless otherwise stated (i.e. CO_2 content).

2.3. Optical Emission Spectroscopy (OES)

OES investigation of the plasma characteristics was carried out using a HORIBA JobinYvon spectrometer (wavelength range of 350 nm - 800 nm) with a high resolution cryogenic CCD detector Symphony. Spectrometer was connected to the chamber by fiber optics. Focus of the fiber optics was aimed at the central plasma zone above the substrate.

2.4. NCD film characterisation techniques

Grown films were investigated with the following techniques:

Raman spectroscopy was carried out at room temperature using a Renishaw InVia Raman Microscope with the following conditions: Wavelength = 488 nm (25 mW), x50 Olympus objective, 65 µm slits, spot focus, Grating = 2400 l/mm.

The topography of the grown layers was investigated by atomic force microscopy (AFM). The AFM measurements were performed with a NTEGRA Prima NT MDT system under ambient conditions. The AFM measurements on layers were performed using the semi contact (tapping) mode. The sample was scanned under the soft HA_NC Etalon Tip type of probe. The tapping mode consisted of oscillating the cantilever at its resonance frequency (111 kHz, amplitude 0.25V) and “tapping” the tip on the surface during scanning.

Secondary electron images were produced of grown films using a FEI Quanta 3D FEG which combines high resolution scanning electron microscope with focused ion beam (DualBeam).

Ellipsometry was carried out using a VASE ellipsometer (Woollam) with a wavelength range of 190nm – 2400nm and an angle of incidence ranging from 20° to 90°.

Samples were characterized ex situ by X-ray photoelectron spectroscopy (XPS) in an apparatus equipped with a nine-channel hemispherical analyzer Phoibos 150 and a dual nonmonochromatized Mg/Al X-ray source. We used Mg K_α line for our experiments, and analyzer operated in a constant analyzer energy mode applying the pass energy of 10 eV, giving a total resolution 0.9 eV.

3. RESULTS AND DISCUSSION

3.1. Plasma characteristics and Optical emission spectroscopy (OES)

OES investigation of the plasma revealed that unlike classical systems the C2 and CH bands, observed typically in the pressure range of 50-200 mbar with MW powers typically of several kW over a 2 inch-substrate, are not present in our PELMWCVD plasmas [7]. As reported in previous work [8] during PELMWCVD growth the concentration of atomic hydrogen was also found to be higher for plasmas with CO_2 addition. An emission spectrum from the presented apparatus is illustrated in

Figure 3, showing that with CO_2 addition we observed three bands with C-O vibrations with wavelengths at 483.5, 519.5 and 560.8 nm. Atomic hydrogen lines (H_α, H_β, H_γ, H_δ) and also the hydrogen molecular band around 600 nm are visible in the measured spectra. No CN related bands were observed suggesting that the system has a low N impurity content. The use of a CO_2 plasma chemistry was based on the publication [1], which was used to prepare films resembling UNCD. However in our approach, by using pulsed plasmas and by modifying the gas chemistry (we use factor 5 higher concentrations) we were able to deposit NCD thin films. The key issues are the hydrogen plasma etching in the off period of the duty cycle and using very high repetition rates which are matched to the atomic H recombination rate at low pressures, allowing a constant high atomic H concentration. The plasma is of a blue-violet color, as characterised by the H excitation spectra (see Figure 3), similar to high pressure MW plasmas, however it is very diffuse and allows coating of 3D objects easily. The plasma density is estimated on our calculations, using the model of linear MW absorption and the known value for the cutoff plasma density for the linear antenna plasmas [1]. In reality we expect that the plasma density is higher, than as already demonstrated [1].

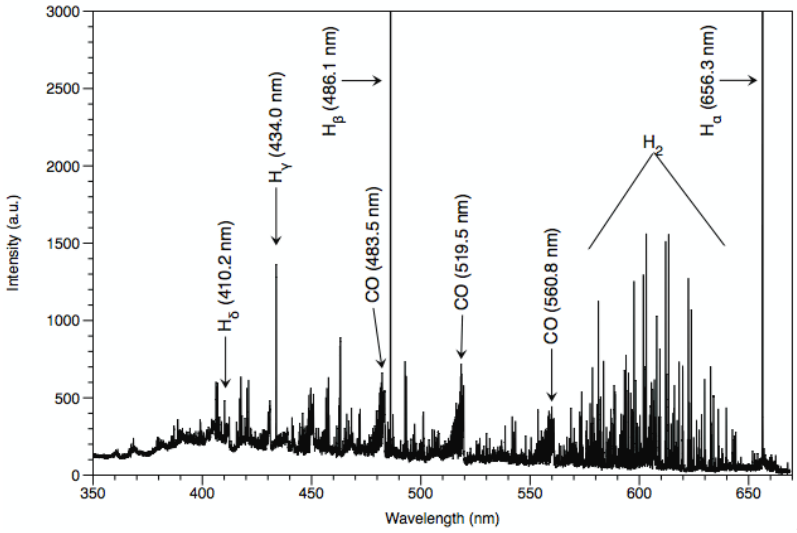

Figure 3, OES spectrum for $CH_4 + H_2 + CO_2$ plasma from PELMCVD apparatus

3.2. Raman spectroscopy

Using Raman spectroscopy, peaks relating to diamond growth (sp^3) and graphitic or amorphous carbon (sp^2) were detected for all layers investigated. It was found that the addition of CO_2 to process gases significantly improved the intensity and width of the sp^3 Raman peak whilst increasing the sp^3 / sp^2 ratio (see

Figure 4). However, when the ratio of CO_2 was greater than that of CH_4 the sp^3 / sp^2 ratio began to decrease. We suggest this increase of sp^2 content with CO_2 concentration is due to saturation of CH species in the plasma on the account of CO_x and CO_XH_Y species, causing an increase in the formation of sp^2. This effect has been studied in detail. Also, as overall flow rates were kept the same, the increase in CO_2 content lead to a relative reduction in H_2 content (as CH_4 was kept constant) leading to a reduction in atomic H in the plasma. With a reduction in atomic H we can expect a reduction in the abstraction and etch rates. Also reduced is the stabilisation of sp^3 bonds on the diamond surface by the H, which will lead to an increase in the sp^2 content and also a

reduction in growth rate (as observed in Table 1). The reduction of atomic H for the highest CO_2 ratios was observed by OES in our measurements.

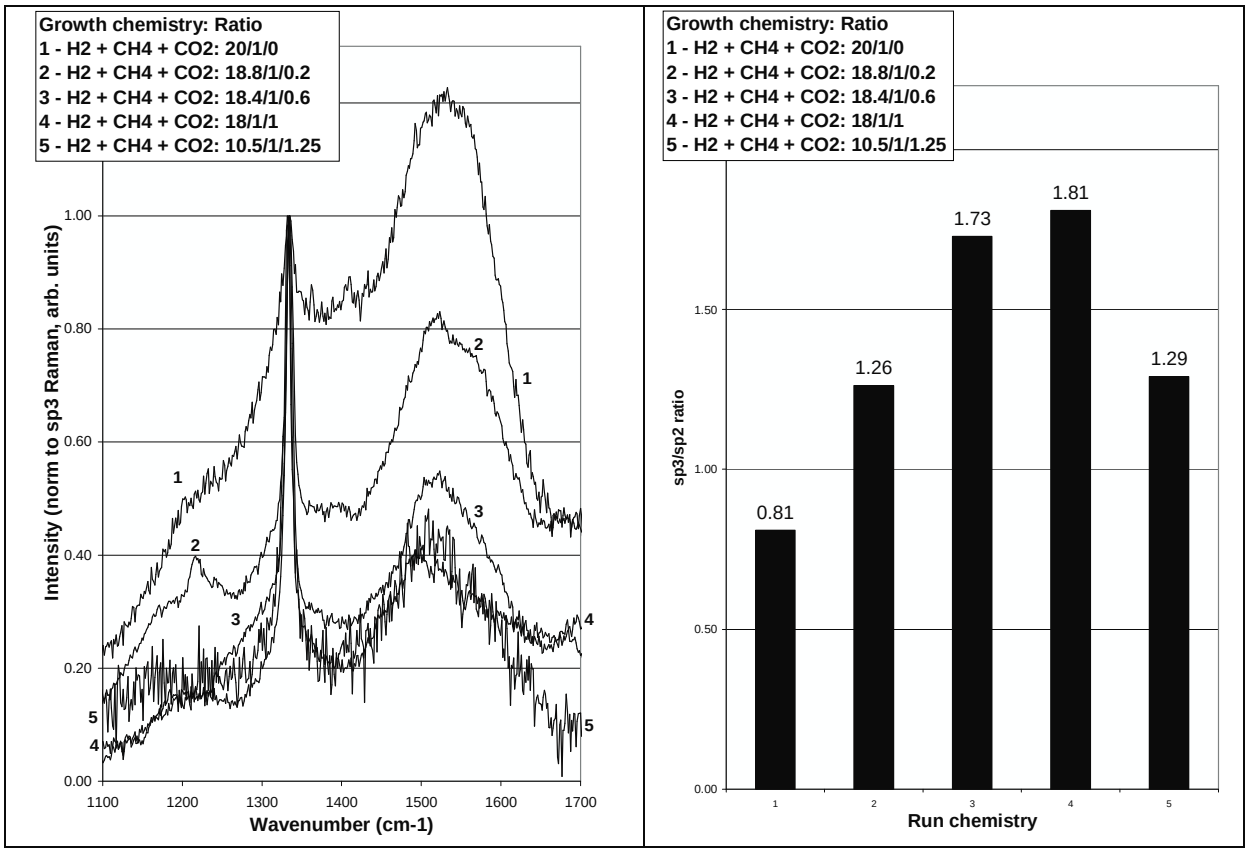

Figure 4, 488nm Raman spectroscopy of NCD layers showing improvement of sp^3 content and reduction of sp^2 content with the addition of CO_2.

3.3. Atomic force microscopy (AFM)

Investigation of grown NCD layers by AFM found that for all reported depositions a continuous layer had been formed in seeded areas (see

Figure 5). Substrates were purposely prepared with unseeded areas to enable measurement of the NCD layer thickness (see: Table 1). It was found that growth rates are enhanced in continuous mode and with the addition of CO_2. However, when the ratio of CO_2 was greater than that of CH_4 the growth rate decreases, this is in accordance with the observed reduction of atomic H. Growth rates were also found to be enhanced at higher growth pressures.

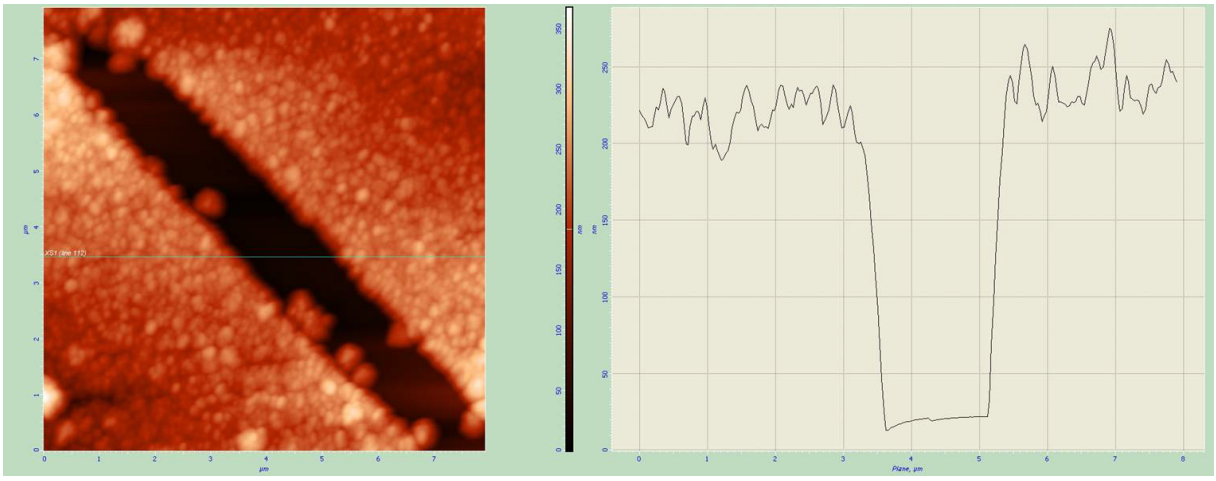

Figure 5, 8µm x 8µm AFM scan of NCD layer showing no growth in unseeded area, step height is 200nm

3.4. Scanning Electron Microscopy (SEM)

SEM investigation was used to evaluate coverage, crystal size, crystal shape and growth rates of all presented NCD layers. Coverage of seeded areas was found to be good for all layers with no holes. The addition of CO_2 to process gases resulted in larger crystal size and also increased crystalline structure when compared with NCD layers grown with no CO_2 (see Figure 6 &

Figure 7). Cross section images revealed a columnar structure to the layers and therefore confirming NCD films. Measured growth rates are presented in Table 1. These growth rates confirm the same trends as in the AFM findings.

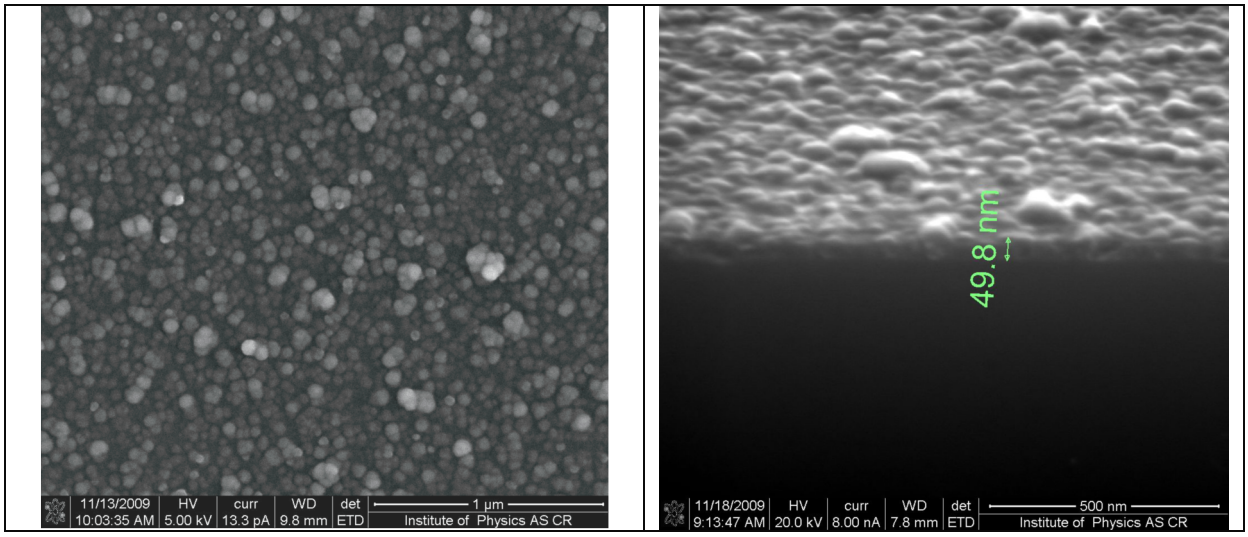

Figure 6, SEM images (plan & cross-sectional) of NCD layer grown with no CO_2 addition

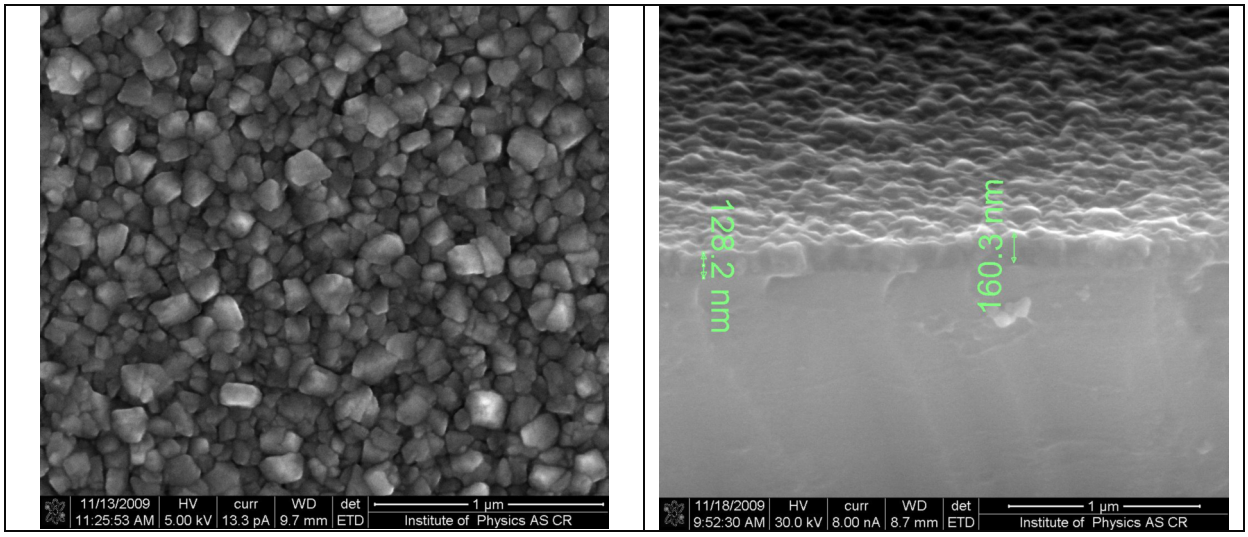

Figure 7, SEM images (plan & cross-sectional) of NCD layer grown with CO_2 addition

3.5. Ellipsometry

Using the model of RMS / NCD layer / SiO_2 layer / Si layer - ellipsometry confirmed that growth rates were enhanced with the addition of CO_2. Refractive index (n) of layers was found to range from 2.20 (400nm) to 3.15 (600nm).

3.6. X-ray photoelectron spectroscopy (XPS)

No contributions of Si were detected in our films which means that the substrate is continuously covered in the measured area which was approximately 5 mm in diameter. Samples prepared by AC method exhibited lower O 1s contribution in comparison with samples prepared by DC way. By measuring detailed spectra of C 1s and O 1s core levels in two configurations - at a normal emission and at 60 deg with respect to the surface normal. On DC samples oxygen is homogenously distributed in the examined layer, while for AC sample is clear that oxygen is present mainly on the surface (peak area ratio for normal and 60 deg emission changed from 0.7 to 1.2).

Process gas ratio			**Growth rate (nm/hr)**			**RMS (nm)**		**Refractive Index**	
H_2	**CH_4**	**CO_2**	**AFM**	**SEM**	**Ellipsometry**	**AFM**	**Ellipsometry**	**n @ 400nm**	**n @ 600nm**
20	1	0	6.25	6.25	7.16	8	20.1	na	2.00
18.8	1	0.2	15.56	14.94	12.11	11.39	23.3	2.40	2.20
18.4	1	0.6	17.50	16.38	16.51	14.78	25.7	na	2.31
18	1	1	10.00	7.63	4.25	11.6	27.3	2.20	2.50
10.25	1	1.25	4.38	na	0.25	6.8	25.7	2.90	3.15

Table 1 Calculated growth rates from AFM, SEM & Ellipsometry for various growth conditions

4. CONCLUSION

A unique PELAMWCVD apparatus working with pulsed plasmas at high frequency (10 kHz), 2 x 10 kW maximum power input and a growth area of 30 x 50 cm was built allowing exploration of non-linear MW absorption plasma chemistry. Suitable low pressure plasma-chemical processes in H_2 + CH_4 + CO_2 gas mixture for enhanced diamond growth rates (20 nm/h) were established for low plasma power densities (4 W/cm^2 compared to > 100 W/cm^2 for classical MW plasma). Columnar i.e. NCD films with low sp2 (~ 4 % for 100nm), low Rms (7-15nm) and index of refraction of ~ 2.4 were prepared.

ACKNOWLEDGEMENTS

Thanks to Dr. Masataka Hasegawa from AIST Japan for fruitful discussions. Financial support from the Academy of Sciences of the Czech Republic (grants KAN200100801, KAN300100801, KAN301370701 & KAN400480701), the European R&D projects FP7 ITN Grant No. 238201 (MATCON) and COST MP0901 (NanoTP) is gratefully acknowledged.

REFERENCES

1. Tsugawa K, Ishihara M, Kim J, Hasegawa M and Koga Y 2006 *New Diamond and Frontier Carbon Technology*,**16**, No.6
2. James E, Butler J, Anirudha V Sumant 2008 *Chemical Vapor Deposition*, Vol: **14**, pp: 145 - 160
3. Nesladek M, Tromson D, Mer C, et al. 2006 *Applied Physics Letters*, Vol: **88**, Issue: 23, Article No: 232111
4. Daenen M, Zhang L, Erni R, et al. 2009 *Advanced Materials*, Vol: **21**, Issue: 6 pp: 670 (2009)
5. Mares JJ, Hubik P, Kristofik J, et al, 2006 *Applied Physics Letters*, Vol: **88**, Issue: 9, Article No: 092107
6. Vandevelde T, Wu T D, et al. 1999 *Thin Solid Films*, Vol: **340** pp: 159 - 163
7. Vandevelde T, Nesladek M, Quaeyhaegens C, et al, 1997 *Thin Solid Films*, Vol: **308**, pp: 154 – 158
8. Elliot M, May P, et al. 2000 *Diamond and Related Materials*, Vol: **9** pp: 311 – 316