ENHANCED GROWTH RATE OF DIAMOND FILMS AT LOW TEMPERATURE IN FOCUSED MICROWAVE PLASMA SYSTEM

Oleg BABČENKO, Irena BYDŽOVSKÁ, Jan FAIT, Ekaterina SHAGIEVA, Lukáš ONDIČ, Alexander KROMKA

Institute of Physics of the Czech Academy of Sciences, Prague, Czech Republic, EU,
babcenko@fzu.cz, *fait@fzu.cz*, *shagieva@fzu.cz*, *bydzovska@fzu.cz*, *ondic@fzu.cz*, *kromka@fzu.cz*

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Abstract

Diamond films are multifunctional materials with a wide range of extraordinary properties and a high application potential in various fields. In this work, we investigate the low temperature (< 500 °C) diamond films chemical vapor deposition on fused silica substrates realized in two different focused microwave plasma systems, i.e. a multimode clamshell cavity reactor (MCC) and a rotational ellipsoid cavity (REC) reactor. During the experiments, the methane to hydrogen ratio, in the hydrogen-rich process gas mixture, varied from 1 % to 15 % for MCC and from 1 % to 9 % for the REC reactor. For both deposition systems, the methane increase led to an increase in the diamond growth rate, e.g. it raised at least by a factor of 2.6 for the MCC reactor. Furthermore, the MCC reactor also allowed the growth of well-shaped diamond crystals at a methane to hydrogen ratio as high as 15 %. This finding is in good agreement with the Raman shift measurements, which also revealed a low content of non-diamond phases in the films making the MCC reactor more preferential for industrial uses. Moreover, the enhanced diamond growth at low temperatures is further advantageous for overcoating fused silica as well as thermally sensitive substrates which altogether opens new vistas for diamond application in optically related fields (optical elements, photonic crystals, sensors).

Keywords: Well-faceted diamonds, low temperature deposition, high growth rate, low non-diamond content, focused plasma

1. INTRODUCTION

Diamond is a material with a wide range of outstanding properties, such as high hardness and abrasion resistance, wide band gap, broad optical transparency, high thermal conductivity, high chemical stability, etc., potentially attractive for numerous applications [1,2]. Unfortunately, technological limitations, so far, hinder large monocrystalline diamond fabrication. In contrast, diamond films are less limited in terms of the large area synthesis [2,3]. Therefore, diamond films are investigated in various research areas as protective coatings, heat spreaders or chemically stable electrodes, or even opto-electronically active parts of sensors or complex optoelectronic devices including photonic structures, quantum devices, etc. [1,2,4].

Although diamond films are generally considered more flexible concerning the integration with other materials, the studies related to an adjustment of diamond deposition processes to the specific needs are still essential. For instance, diamond film deposition on thermally or chemically sensitive substrates requires the deposition conditions tailoring and/or application of protective layers [2,4,5]. In the case of diamond growth on glass or quartz substrates, the issue of thick diamond layer delamination due to thermal expansion coefficients mismatch and the appearance of residual stress needs to be taken into account [2,5]. Modification of substrate surface morphology or additional stress-relaxation layers as well as decrease of deposition temperature are the typical solutions for the mentioned issue [5-7]. Here it needs to be noted that for electronic applications the electrical properties of the resulting heterostructure are important while optical applications required optical properties preserving [1,2,6-9]. Moreover, the low deposition temperature means a decreased diamond growth rate that prolongs deposition time and/or changes the growth kinetics [5,10,11]. A higher amount of carbon-based species in the growth mixture commonly enhances the growth rate. However, it increases not only the amount of non-diamond content in the grown layers but carbon deposits on the chamber walls which often lead to plasma instability [2,9-11].

In this work, we realize the series of experiments on the low temperature (< 500 °C) diamond film chemical vapor deposition (CVD) at different methane concentrations. We investigate the diamond growth on fused silica substrates from H_2/CH_4 process gas mixture in two different focused microwave plasma systems, i.e. a multimode clamshell cavity reactor and a rotational ellipsoid cavity reactor. To facilitate the diamond growth in its early stage, i.e. beginning of the deposition process, thin diamond layers were pre-deposited on fused silica wafers in the large area linear antenna pulsed microwave plasma system [5,12], which were then used as the starting substrates for this study.

2. EXPERIMENT

The experiments with a focus on the low temperature (< 500 °C) diamond film CVD at different methane concentrations were realized in the multimode clamshell cavity (MCC) reactor (SDS6K, Seki Diamond Systems) and rotational ellipsoid cavity (REC) reactor (P6, Diamond Materials GmbH), i.e. two types of focused microwave (MW) plasma CVD system [1,3]. The fused silica (type JGS1) wafers cut to 1x1 cm^2 pieces were used as substrates. Before the diamond CVD process, substrates were seeded in an ultrasonic bath for 40 min using the water-based ultra-dispersed diamond powder suspension (NanoAmando, nominal particle size 5 nm), to receive high diamond nucleation densities [12,13]. Next, the set of samples was coated by the thin (95 nm) diamond layer in the large area linear antenna pulsed MW plasma system (AK 400, Roth & Rau) [5,12]. The 12 h CVD process was realized in the $H_2/CO_2/CH_4$ gas mixture (gas flows 200/20/5 sccm) at a pressure of 15 Pa (0.15 mbar) and microwave power 2x1800 W delivered from two sides of antennas. The average substrate temperature during the process was kept at 420 °C by resistive heating of the substrate holder. These samples, labeled as SD, were then used for diamond CVD growth in focused plasma systems while only seeded fused silica substrates, labeled as SN, were used in the experiments as reference.

The series of experiments in the MCC reactor was realized at the following deposition conditions: H_2/CH_4 process gas mixture with an amount of methane varied from 1 to 15 % of hydrogen flow (300 sccm), pressure 4 kPa (30 Torr), microwave power 2000 W and temperature maintained around 450-460 °C. The time of each CVD process was adjusted according to the results of preliminary experiments and methane amount in the mixture in order to have diamond layers of the total thickness 340±14 nm.

The diamond films deposition conditions in the REC reactor were as followed: H_2/CH_4 process gas mixture with the amount of methane varied from 1 to 9 % of hydrogen flow (300 sccm), pressure 3 kPa (30 mbar), microwave power 1500 W and temperature around 450 °C. As for MCC reactor, the time of each CVD process was adjusted according to the earlier experiments and methane amount in a mixture in order to have diamond layers of the total thickness 230±13 nm.

The diamond films thickness for experiments was evaluated by a non-destructive method using the home-made reflectance interferometry setup [12]. The grown films surface morphology was characterized by the field-emission scanning electron microscopy (FE-SEM, Tescan MAIA3). The grown films composition was studied by the Raman spectroscopy (Renishaw InVia Reflex Raman microscope) using the laser with an excitation wavelength of 442 nm.

3. RESULTS AND DISCUSSION

The typical morphology (investigated by SEM) and Raman spectrum of pre-grown diamond layer on SD samples are shown in **Figure 1**. The pre-grown layer is uniform and consisted of features with size less than

100 nm and no clear facets (**Figure 1a**) reported earlier [5]. The peaks and bands observed in the Raman spectrum of SD sample (**Figure 1b**) were attributed to: characteristic diamond peak centered at 1332 cm^{-1}, D-band centered at 1355 cm^{-1}, the G-band around 1590 cm^{-1} and a weak band around 1490 cm^{-1} the most probably related to transpolyacetylene (TPA) residues at grain boundaries [13-15].

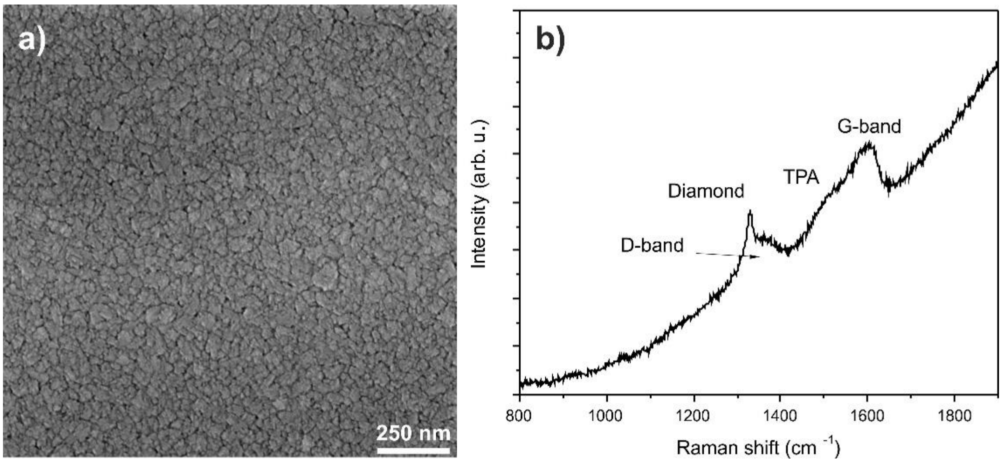

Figure 1 The SEM images of pre-grown diamond layer morphology (a) and measured Raman spectrum (b).

The morphology of the diamond films grown on SD samples (fused silica with thin pre-grown diamond layer) at different methane to hydrogen ratios in the MCC reactor are shown in **Figure 2**. It can be seen that the diamond layer grown from mixture with CH_4/H_2 ratio 1 % (low methane concentration) is not uniform, although consisted of fine-grained crystallites. In the grown layer the large (up to 500 nm) diamond crystallites are protrude from the layer of smaller (150-250 nm) crystallites with randomly distributed voids in between. Increasing CH_4/H_2 ratio up to 6 % resulted in a slight decrease of crystal sizes while voids in layer disappeared. Further increase of CH_4/H_2 ratio to 15 % decreased the crystal sizes down to approximately 50 and 400 nm for small and large crystals, respectively. Nevertheless, the crystallites remain well-faceted and distinguishable. The decreasing of diamond crystal sizes is attributed to the shift of diamond growth kinetic toward the higher diamond re-nucleation yields [2,5,13]. Whilst, high plasma density and still enough high amounts of atomic hydrogen promote the lateral diamond growth [3].

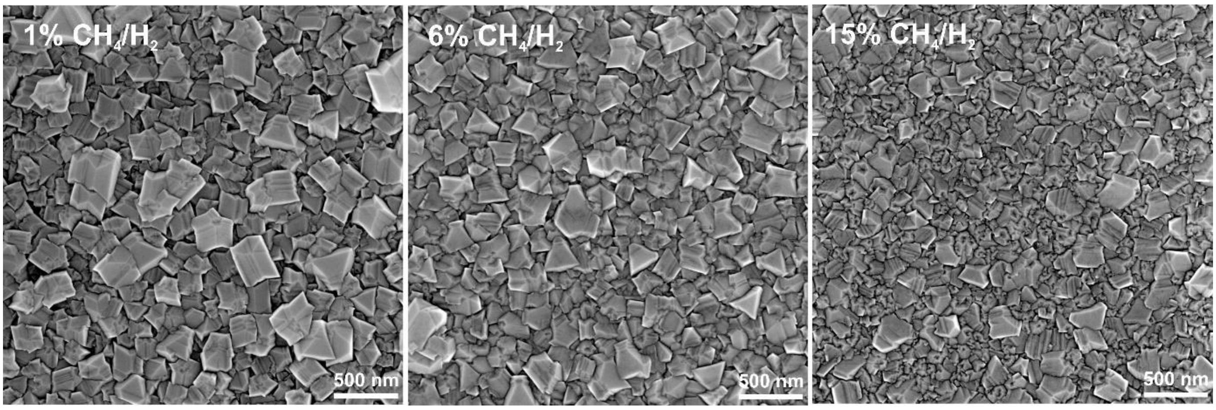

Figure 2 The SEM images of diamond films grown on SD samples at different methane to hydrogen ratios in the MCC reactor.

Raman spectra from layers grown on SD samples in the MCC reactor (**Figure 3a**) reveal characteristic features of thin diamond films. In particular, the spectrum is dominated by a diamond peak centered at 1332 cm^{-1}, and reveals also the D-band at 1355 cm^{-1}, the G-band around 1590 cm^{-1} and two bands centered at 1490 cm^{-1} and a weaker band at 1150 cm^{-1} attributed to TPA located at grain boundaries [13-15]. The best signal-to-noise ratio and the narrower diamond peak were observed for the diamond film grown at 1 % of CH_4/H_2. However, all spectra from diamond layers grown in the MCC reactor normalized to diamond peak (not shown) were very similar and demonstrated a very low amount of non-diamond carbon phases (with slight variation of TPA and G-band contribution). It agrees with the SEM observation of diamond films with well-faceted crystals in CH_4/H_2 ratio range from 1 to 15 %.

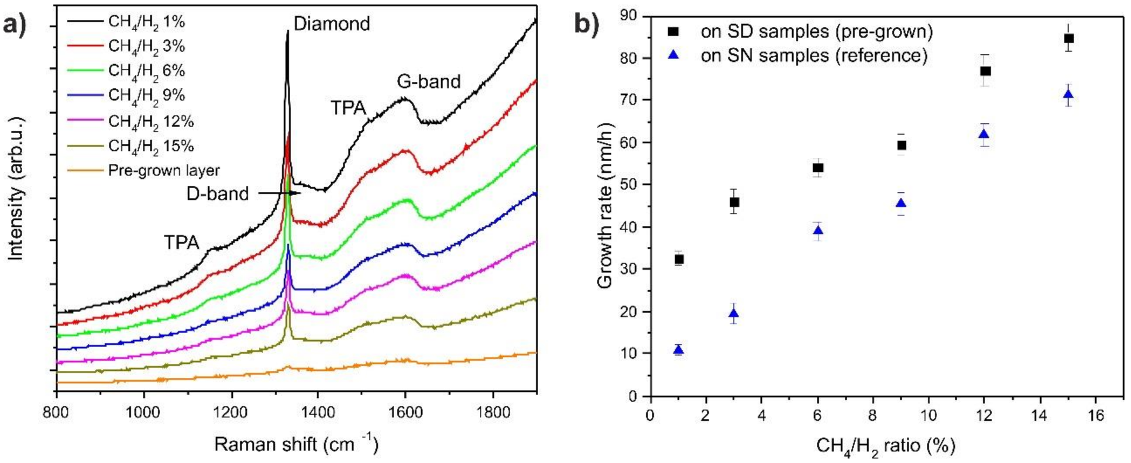

Figure 3 As-measured Raman spectra of layers grown on SD samples (a) and the growth rates of diamond films grown on SD and SN samples (b) at different methane to hydrogen ratios in the MCC reactor.

Concerning the growth rate (**Figure 3b**), it monotonically increases for both sample types, i.e. SD samples with the pre-grown diamond layer and SN - the seeded reference samples, respectively. The increase in the growth rate is attributed to a higher amount of carbon growth species due to used higher amount of methane [3,11]. The growth rate for SD samples raised from 32.6 to 85 nm/h (i.e. the enhancement factor of 2.6) for the increase of CH_4/H_2 ratio from 1 % to 15 %. The lower growth rate values observed for the reference SN samples (from 11 nm/h for 1 % CH_4/H_2 to 71.3 nm/h for 15 % CH_4/H_2) are affected by the prolonged incubation time (also known as delay time) at the early stage of the diamond CVD growth [6]. It is known that after passing that delay time the growth rate values on such samples as SN will increase [6] while using of SD samples with the pre-grown diamond layers allow to significantly shorten the incubation period. Finally, it needs to be noted that at higher CH_4/H_2 ratio the delay time is shorter which is indicated by the decreasing of the difference between growth rate for SN and SD samples with increase of CH_4/H_2 ratio. Keeping in mind the indication on the re-nucleation yields increasing and growth kinetic change the growth rate trend should not be linearized.

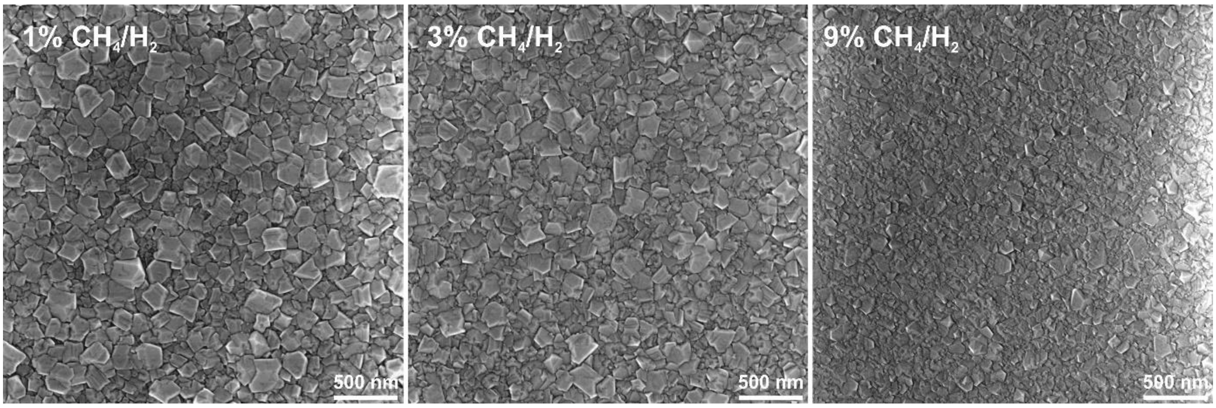

Figure 4 The SEM images of diamond films grown on SD samples at different methane to hydrogen ratios in the REC reactor.

Surface morphologies of diamond films grown on SD samples at different methane to hydrogen ratios in the REC reactor are shown in **Figure 4**. In the case of low temperature diamond deposition with a CH_4/H_2 ratio from 1 to 3 % in the REC reactor, the diamond films consisted of randomly oriented, densely packed, well-faceted diamond crystallites with sizes from 50 nm to 300 nm. With the increase of methane to hydrogen ratio to 9% the amount of the small-sized (50 nm and smaller) diamond crystallites also increases, while crystallites with sizes above 150 nm were not observable, which should be attributed to the increase in the diamond re-nucleation rate [2,5,13]. Contrary to the MCC reactor (**Figure 2**), the shift of the growth kinetic towards the high re-nucleation yield in the REC reactor begins at much lower methane concentrations, which is more or less related to differences in the reactor designs [3].

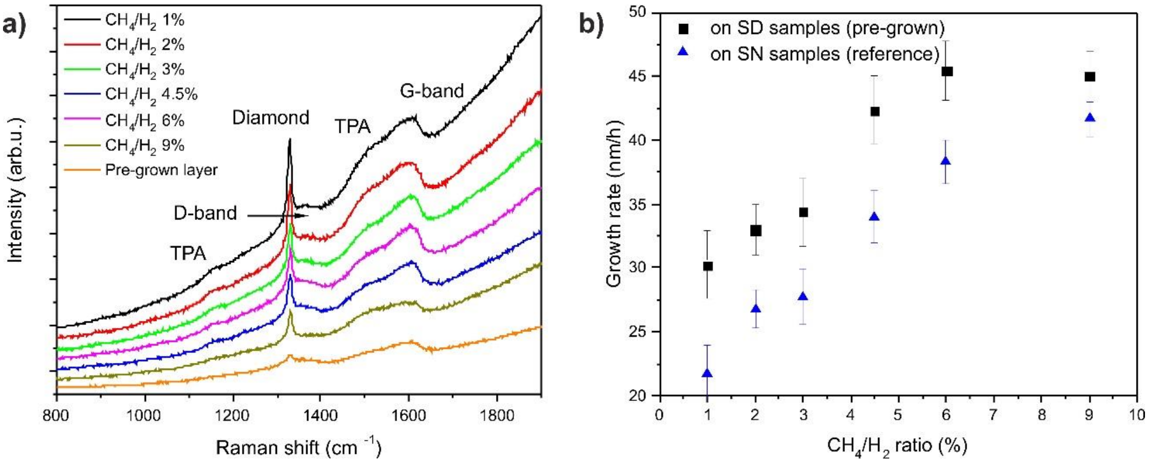

Figure 5 As-measured Raman spectra of layers grown on SD samples (a) and growth rates of diamond films grown on SD and SN samples (b) at different methane to hydrogen ratios in the REC reactor.

Raman spectra of samples grown in the REC reactor are depicted in **Figure 5a.** Similarly to the MCC reactor, all spectra reveal thin diamond films features consisting of the diamond peak (1332 cm^{-1}), D- and G-bands (1355 cm^{-1} and 1590 cm^{-1} respectively), and TPA bands (1490 cm^{-1} and 1150 cm^{-1}) [13-15]. The spectra normalized to diamond peak (not shown) reveal increase of non-diamond phases with the increase of the methane amount in the mixture. Nevertheless, the diamond peak in spectra remains clearly detectable for all used CH_4/H_2 ratios which agrees with observation of Catledge et al. for temperature 425 °C [10]. Therefore, we believe that our findings indicate on reasonable non-diamond carbon species etching during the CVD process in REC reactor at temperature around 450 °C up to CH_4/H_2 ratio at least 9 %. The growth rate (**Figure 5b**) for SD samples increased from 30.2 to 45.4 nm/h with methane to hydrogen ratio increase from 1 % up to 6 %, and then stays close to the saturated value of 45 nm/h for 9 % CH_4/H_2. The maximum enhancement of the growth rate in the REC reactor is 1.5 found for 6 % of methane to hydrogen ratio. For SN samples the growth rate increases from 21.7 to 41.7 nm/h with CH_4/H_2 ratio increase from 1 % up to 9 %. Similar to previous, the slightly lower growth rate values for SN samples are attributed to delay time at the early stage of the diamond CVD [6]. However, in contrast with the MCC reactor, it seems that the growth rate trend for REC reactor approaches the saturation at CH_4/H_2 ratio above 6%. It corresponds to the SEM observations (**Figure 4)** indicated the diamond growth kinetic changing and the re-nucleation yield increasing for higher CH_4/H_2 ratio.

Finally, it should be noted, that for both reactors types the high methane concentration in the gas mixtures (CH_4/H_2 ratio for MCC reactor from 15 % and for REC reactor from 6 %) resulted in increased carbon-based film deposition on the chamber walls and quartz MW window which negatively influenced the plasma stability [2,3]. This is especially more critical for the REC reactor, where carbon deposit on the quartz jell bar suppresses the microwave propagation into the chamber and often results in the plasma ball movement ("*jump*") to the quartz bell jar, its later overheating and destroying. Therefore, although the further growth rate increase with increase of CH_4/H_2 ratio in MCC reactor is possible, the experiments on the diamond growth with higher methane amount in the mixture were estimated as unsafe because endanger the systems functionality.

4. CONCLUSION

We investigated the low temperature (< 500 °C) diamond film deposition on fused silica in the hydrogen-rich process gas mixtures in two different focused microwave plasma systems. For both deposition systems we observed an increase in the diamond growth rate with the increase of methane amount in the growth mixture. Moreover, during CVD with high methane to hydrogen ratio we also observed increase of carbon films deposit on chamber walls which is a limiting factor for the long-term deposition process. The diamond growth rate on the substrates with pre-deposited (growth enhancing) diamond layers for CVD in MCC reactor increases by factor of 2.6 with the methane to hydrogen ratio increase from 1 % to 15 %. For REC reactor the growth rate on the same type of substrates increases by factor 1.5 with the methane to hydrogen ratio increase from 1 % to 6 % and then saturates. The Raman shift measurements on diamond films grown in the MCC reactor with CH_4/H_2 ratio in range from 1 % to 15 % revealed a low content of non-diamond phases in all grown layers. It corresponds with the SEM observation of diamond films with well-shaped crystals in all cases. On the other hand, the CH_4/H_2 ratio increasing from 1 % to 9 % for REC reactor resulted to evident increase in number of diamond crystals with small sizes and also increase in amount of non-diamond carbon in the films. It was attributed to the change of diamond film growth kinetic and increase of the diamond re-nucleation yield that for REC reactor begins at lower methane concentrations than for MCC reactor. Considering all mentioned observation, we believe that the design of the MCC reactor is more favorable for well-facetted diamond films deposition at high CH_4/H_2 ratio than REC reactor. We proposed, that the enhanced diamond growth rate at low temperatures in MCC system will be advantageous for overcoating of fused silica, thermally sensitive substrates, e.g. optical elements, photonic crystals, sensors, etc.

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