

## INFLUENCE OF THE NUCLEATION PROCESS ON THE PROPERTIES OF BORON DOPED DIAMOND FILMS DEPOSITED ON STRUCTURED SILICON

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### Abstract

We report here on the preparation and characterization of polycrystalline boron doped diamond (BDD) thin films grown on structured silicon substrates using hot filament chemical vapor deposition (HFCVD) method. The BDD layers were grown in CH<sub>4</sub> / H<sub>2</sub> gas mixture with trimethylboron (TMB) addition. Before diamond depositions, different nucleation processes were applied (diamond nanoparticles in deionized water or methanol, with/without oxygen plasma treatment). Layers with thicknesses from 0.2 to 1 μm were deposited at varied ratios of B / C and CH<sub>4</sub> / H<sub>2</sub> in the CH<sub>4</sub> / H<sub>2</sub> / TMB gas mixture. Scanning electron microscopy (SEM) was used to analyze the samples. Oxygen plasma pretreatment was found as crucial for successful coating of the whole silicon pillars by diamond film including the bottom part. For some of the pretreatment methods (i.e. short nucleation time, < 5min), the HFCVD process resulted in formation of BDD caps on the top of silicon pillars.

**Keywords:** boron doped diamond, reactive ion etching, black silicon, chemical vapor deposition

### 1. INTRODUCTION

The highest hardness and thermal conductivity, chemical inertness, corrosion resistance, biocompatibility, wide electrochemical potential window, low electrochemical background current and optical transparency are the main reasons of wide use of diamond in industry and interest in research including electrochemistry [1]. At the end of the twentieth century, production of boron-doped diamond by chemical vapor deposition (CVD) was invented and new applications of diamond have been found [2]. Boron doping leads to better conductivity that has positive impact mainly on the current density, sensitivity and selectivity of the BDD electrodes used for electrochemical applications. Nowadays, the most perspective electrochemical applications of BDD are the treatment and disinfection of waste water, production of strong oxidizers, bioelectrochemical, electrocatalytical, spectroelectrochemical, and electroanalytical applications [3], [4]. Electrochemical reactions perform mostly at the interface between electrolyte solutions and the electrodes surfaces. Therefore, the modification of the electrode surface morphology is a key factor, which may be used to increase the active electrode area and radial diffusion on the edges of structures. When the size of the electro - active area is scaled down, the mass transport to the active element will be enhanced by hemispherical diffusion causing the microelectrode to approach a steady - state limiting current [6]. On the other hand, an enlargement of the diamond - based sensors active area by increase of the surface - to - volume ratio leads to an increase of sensitivity and selectivity [7]. Yoshimura et al. [8] published the fabrication method of diamond nano - honeycomb structures by using oxygen plasma etching. They observed that by increasing the electrode area the double - layer capacitance increased by factors up to 400.

In our previous work we were focused on nucleation process of diamond layers only by bias enhanced nucleation in HF CVD [10], [11]. We found that this technique is possible to be used only on conductive and

not complicated (cutting tools, flat Si substrates, etc.) 3D substrates. In this study, nucleation parameters of structured and black silicon substrates, such as the process time and solution used in ultrasonic seeding of diamond nanoparticles were optimized. Moreover, deposition parameters of HFCVD (i.e. B / C and CH<sub>4</sub> / H<sub>2</sub> ratio) were optimized to meet the requirements for electrochemical applications including high power electrochemical applications like waste water treatment, where a strong adhesion of BDD to silicon substrate is necessary.

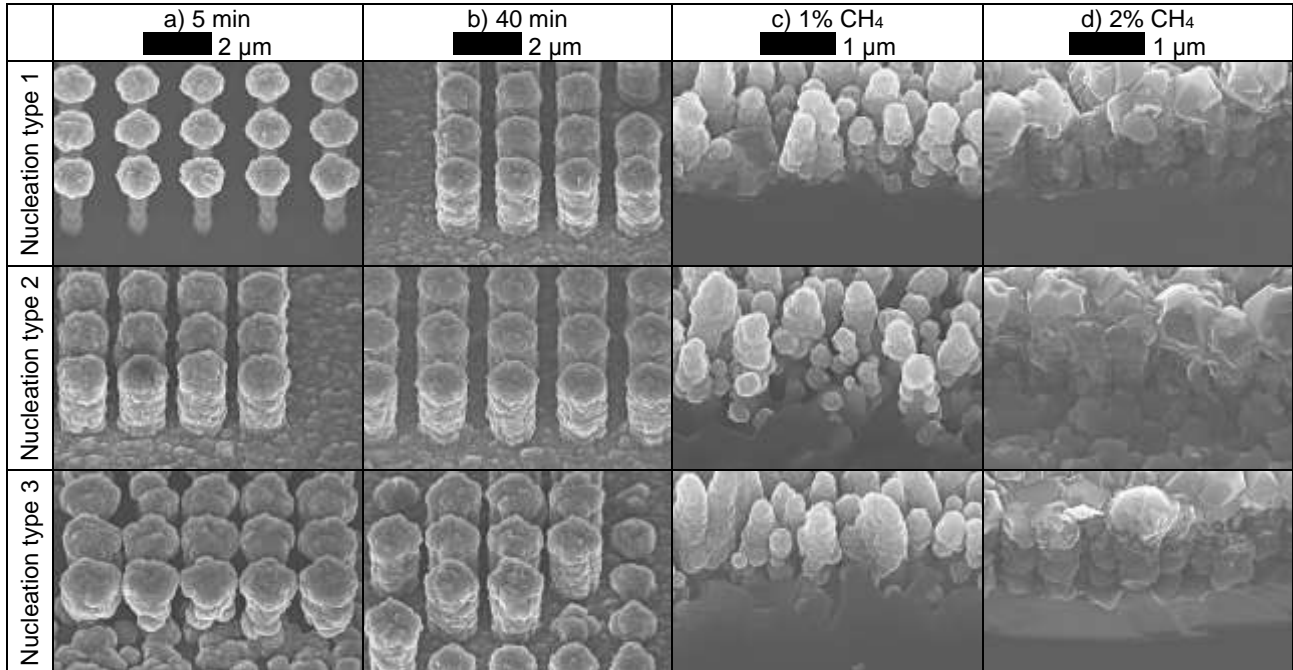
## 2. EXPERIMENTAL PART

Structured N - type 525 μm thick silicon (100) wafers were prepared at Ilmenau University of Technology. Process of structuring consisted of UV lithography and reactive ion etching (RIE) including Bosch technology. In the UV lithography process, a testing mask was used. Etching was realized by Bosch process with SF<sub>6</sub> and C<sub>4</sub>F<sub>8</sub>. The etching speed was 0.8 μm / min. Three series of wafers with specific depths (5 μm, 6.5 μm and 17 μm) were prepared. Etching depth as well as the quality of structures were controlled by a tactile profilometer (Dektak) and scanning electron microscopy (SEM). Black silicon samples were prepared using etching and passivation during structuring. Next steps including cutting of wafers to obtain substrates with area of 1x1 cm<sup>2</sup>, nucleation of substrates and deposition of BDD were done at Slovak University of Technology. Three different types of nucleation process were used before deposition of BDD. Each one was based on ultrasonic seeding of diamond nanoparticles [12]. In the first case (Nucleation type 1), the samples were nucleated in an ultrasonic bath in a solution of 50 mg nanodiamond powder with diameter <10 nm (CAS No. 7782 - 40 - 3, Sigma Aldrich) and 1 000 ml demineralized water (18 MΩ) for 5 or 40 minutes, respectively. In contrast to that, the substrates employed in 'Nucleation type 2' were first treated in oxygen plasma before the ultrasonic seeding to obtain hydrophilic character of the surface. The third type of nucleation (Nucleation type 3) was the same as the first type, only the demineralized water was replaced by methanol. The nucleated substrates were subsequently overgrown with BDD using HFCVD apparatus in a CH<sub>4</sub> / H<sub>2</sub> gas mixture with addition of TMB at process pressure of 3 000 Pa for 120 min. B / C ratios were set up to 4 000 ppm, 8 000 ppm and 10 000 ppm, respectively and the ratio of CH<sub>4</sub> / H<sub>2</sub> was 1 or 2%. Substrate temperature (700 °C ±50 °C) was monitored during the growth process by an infrared pyrometer. Samples were analysed by SEM JEOL 7500F under tilted angle view at 45 degrees.

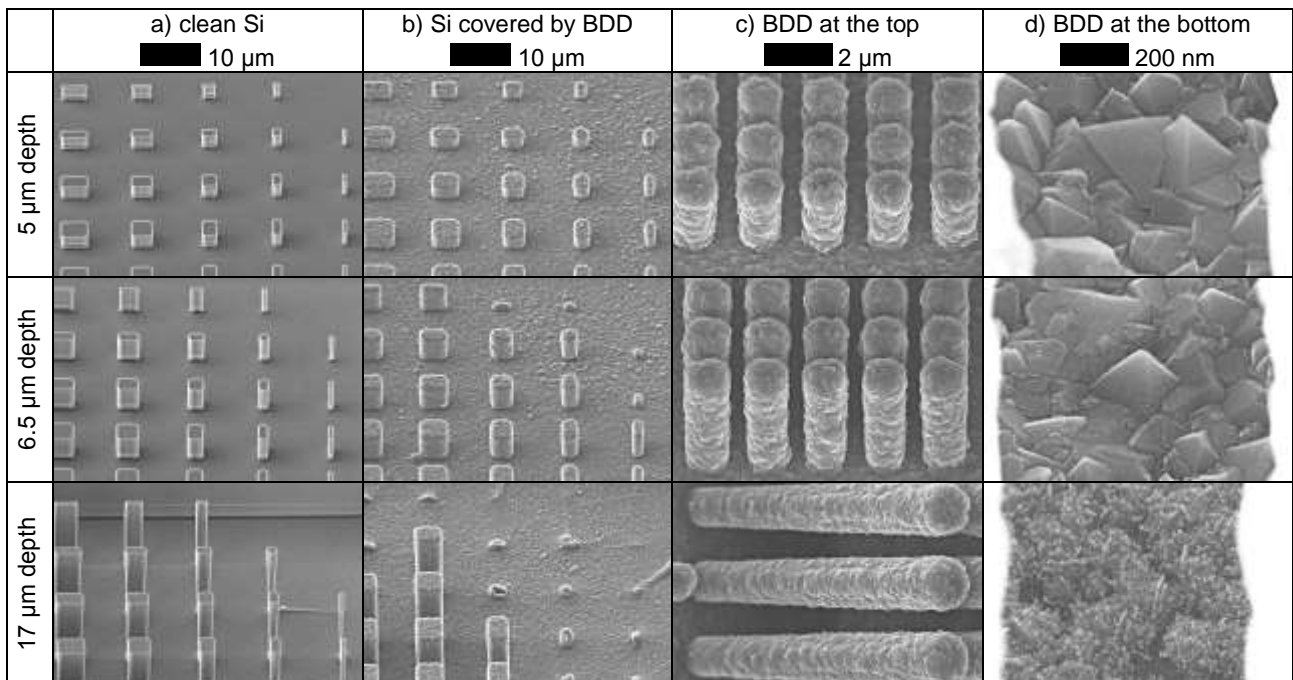
## 3. RESULTS AND DISCUSSION

Fig. 1 shows scanning electron micrographs of BDD layers deposited on the silicon pillars (Fig 1a - b) and on the black silicon (Fig 1c - d) using different nucleation procedures and times. In the case of 40 min nucleation and 2 % CH<sub>4</sub> / H<sub>2</sub> ratio growth, comparable results showing full and homogenous covering of silicon substrate with BDD for all types of nucleation were observed. In the case of 5 minutes nucleation, only after nucleation type 2, full and homogenous covering of silicon substrates with BDD was observed. This phenomenon indicates that, only the silicon substrates treated by oxygen plasma before nucleation process are hydrophilic enough for the water nucleation solution. In the case of silicon pillars array in combination with the Nucleation type 1, only BDD caps on the top of pillars were observed. These structures were observed only on the pillars with diameter less than 5 μm and their presence has been probably caused by a spontaneous growth of the diamond on the edges which usually occurs in case of insufficient or no nucleation. The phenomenon may be interesting for production of P - N junctions with unique properties. As we can see in Fig. 1c - d, a change of the CH<sub>4</sub> / H<sub>2</sub> ratio from 1% to 2% increased the size of diamond grains as well as the thickness of BDD layer. In the case of black silicon substrates, the quality of covering with BDD was also significantly influenced. This indicates that the presence of a higher amount of carbon species in the gas mixture causes a faster growth. The average diamond layer thickness was 200 nm for 1% CH<sub>4</sub> / H<sub>2</sub> ratio and 600 nm for 2% CH<sub>4</sub> / H<sub>2</sub> ratio in the case of silicon pillars. The SEM images did not show an influence of the variation in B / C ratio on the covering and homogeneity of substrates by BDD thin films. The silicon structures with a diameter less than 500 nm were often damaged during the etching process (Fig. 2a). Additional degradation of the thinnest structures could be caused by the impact of

ultrasonic waves during the nucleation process (Fig. 2b). Therefore, a non - ultrasonic nucleation process should be investigated for thin structures with diameter less than 1  $\mu\text{m}$  in future experiments. In Fig. 2d the boron doped diamond grown at the bottom of the comb structures with distance of 1  $\mu\text{m}$  is shown. In the case of 17  $\mu\text{m}$  etching depth, only an insufficient covering by BDD was achieved.



**Fig. 1** SEM images of BDD - coated (B / C = 10 000 ppm) Si structures with different nucleation types and times ( $t_n$ ). Column a), b) BDD on Si pillars, CH<sub>4</sub> / H<sub>2</sub> = 2%,  $t_n$  = 5 min. and 40 min. respectively. Column c), d) cross - section of BDD grown on black silicon,  $t_n$  = 40 min., CH<sub>4</sub> / H<sub>2</sub> = 1% and 2% respectively. Scale bar for each SEM images are shown on the top of column.



**Fig. 2** SEM images of BDD - coated Si structures with different etching depths (i.e. 5, 6.5, 17  $\mu\text{m}$  for first, second and third row, respectively) and with parameters B/C = 10 000 ppm, CH<sub>4</sub> / H<sub>2</sub> = 2% and nucleation time = 40 min. Column a) Si pillars before BDD deposition, b) Si pillars (2 – 5  $\mu\text{m}$ ) with 10  $\mu\text{m}$  gap, c) top of pillars with diameter of 1  $\mu\text{m}$  and 1  $\mu\text{m}$  gap, d) detail of BDD at the bottom of the comb structures. Scale bar for each SEM images are shown on the top of column.

#### 4. CONCLUSION

Summarizing the experimental results, we can assume a good possibility of boron doped diamond thin films deposition on the structured silicon wafers with various structures types and etching depths. All of the substrates nucleated for 40 min and deposited with 2 % CH<sub>4</sub> / H<sub>2</sub> ratio were homogeneously overgrown by high quality continuous BDD. A positive impact of the silicon substrates pre - treatment in oxygen plasma on the BDD homogeneity was observed and led to reduction of nucleation time to 5 minutes. Furthermore, we obtained microcrystalline diamond caps grown on the top of the silicon pillars which are interesting for a future research and could find interesting applications e.g. in photonics.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- [1] LOUNG J. H. T., MALE K. B., GLENNONA J.D., MULA J., Boron-doped diamond electrode: synthesis, characterization, functionalization and analytical applications, *Analyst*, Vol.134, 2009, pp. 1965-1979
- [2] ALFARO M. A. Q., FERRO S., MARTÍNEZ-HUITLE C. A., VONG Y. M., BRAZ,. Boron Doped Diamond Electrode for the Wastewater Treatment *J. Chem. Soc.*, Vol. 17, 2006, pp. 227-236
- [3] ŠVORC L., VOJS M., MICHNIAK P., MARTON M., RIEVAJ M., BUSTIN D., Electrochemical behavior of methamphetamine and its voltammetric determination in biological samples using self-assembled boron-doped diamond electrode, *Journal of Electroanalytical Chemistry*, Vol. 717-718, 2014, pp. 34-40
- [4] BANDŽUCHOVÁ L., ŠVORC L., VOJS M., MARTON M., MICHNIAK P., CHÝLKOVÁ J., Self-assembled sensor based on boron-doped diamond and its application in voltammetric analysis of picloram, *International Journal of Environmental Analytical Chemistry*, Vol. 94, No. 9, 2014, pp. 943-953
- [5] MARTON M., VOJS M., KOTLÁR M., MICHNIAK P., VANČO L., VESELÝ M., REDHAMMER R., Deposition of boron doped diamond and carbon nanomaterials on graphite foam electrodes, *Applied Surface Science*, Vol. 312, 2014, pp. 139-144
- [6] ZHOU., J. ZHI, The application of boron-doped diamond electrodes in amperometric biosensors, *Talanta*, Vol. 79 2009, pp. 1189-1196
- [7] HUPERT M., MUCK A., WANG J., STOTTER J., CVACKOVA Z., HAYMOND Sh., SHOW Y., SWAIN G. M., Conductive diamond thin-films in electrochemistry, *Diamond and Related Materials*, Vol. 12, 2003, pp. 1940–1949
- [8] YOSHIMURA M., HONDA K., UCHIKADO R., KONDO T., RAO T. N., TRYK D.A., FUJISHIMA A., SAKAMOTO Y., YASUI K., MASUDA H., Electrochemical characterization of nanoporous honeycomb diamond electrodes in non-aqueous electrolytes, *Diamond and Related Materials*, Vol. 10, 2001, pp. 620-626.
- [9] MALCHER V., MRŠKA A., KROMKA A., ŠATKA A., JANIK J., Diamond film coated on WC / Co tools by double bias-assisted hot filament CVD, *Current Applied Physics*, Vol. 2, 2002, pp. 201–204.
- [10] IZAK T., MARTON M., VARGA M., VOJS M., VESELY M, REDHAMMER R., MICHALKA M. Bias Enhanced Nucleation of Diamond Thin Films in a Modified HFCVD Reactor, *Vacuum*, Vol. 84, 2009, pp. 49-52.
- [11] VOJS, M., VESELÝ, M., REDHAMMER, R., JANÍK, J., KADLEČÍKOVÁ, M., DANIŠ, T., MARTON, M., MICHALKA, M., ŠUTTA, P. Double bias HF CVD multilayer diamond films on WC-Co cutting tools, *Diamond and Related Materials*, Vol. 14, No. 3-7, 2005, pp. 613-616.
- [12] VARGA M., IŽÁK T., KROMKA A., VESELÝ M., HRUŠKA, K., MICHALKA M. Study of diamond film nucleation by ultrasonic seeding in different solutions, *Central European Journal of Physics*, Vol. 10, No. 1, 2012, pp. 218-224.