(100) SUBSTRATE PROCESSING OPTIMIZATION FOR FABRICATION OF SMOOTH BORON DOPED EPITAXIAL DIAMOND LAYER BY PE CVD

MORTET Vincent[1,2], FEKETE Ladislav[1], ASHCHEULOV Petr[1], TAYLOR Andrew[1,2], HUBÍK Pavel[3], TREMOUILLE David[4,5], BEDEL-PEREIRA Elena[4,5]

[1]Institute of Physics, Academy of Sciences of the Czech Republic, v.v.i, Na Slovance 2, 182 21 Prague 8, Czech Republic, mortetv@fzu.cz; [2]Czech Technical University in Prague, Faculty of Biomedical Engineering, nám. Sítná 3105, 272 01 Prague, Czech Republic; [3]Institute of Physics, Academy of Sciences of the Czech Republic, v.v.i., Cukrovarnická 10, 16200 Prague 6, Czech Republic, [4]LAAS-CNRS, 7 avenue du colonel Roche, BP 54200, 31031 Toulouse Cedex 4, France, [5]Univ. de Toulouse, LAAS, 31400 Toulouse, France.

Abstract

Boron doped diamond layers have been grown in an SEKI AX5010 microwave plasma enhanced chemical vapour deposition system. Effect of surface preparation, i.e. polishing and O2/H2 plasma etching on epitaxial growth on type Ib (100) HPHT synthetic diamonds were investigated. Using optimized substrate preparation, smooth (R_{RMS} ~ 1 nm) boron doped diamond layers with metallic conduction and free of none epitaxial crystallites have been grown with a relatively high growth rate of 3.7 µm/h. Diamond were characterized by optical microscopy, optical profilometry, atomic force microscopy and Hall effect.

Keywords:

Doping; PE CVD; Diamond; Surface treatment; Thin film

1. INTRODUCTION

In addition to low capacitance, high chemical stability, boron-doped diamond has unique wide electrochemical window (3.5 V in aqueous electrolyte) that allows detection of chemical species not measurable using other electrodes. Therefore diamond has become the centre of interests for many electrochemical applications and commercial electrodes are already available. Applications of BDD electrodes are centred on electrochemical analysis in medical diagnostics and wastewater treatment [1, 2] for environmental protection. The behaviour of diamond's electrode is complex and requires careful fabrication process and detailed analysis to develop high end value applications. Polycrystalline diamond layers have large amount of grain boundaries and cannot be used for these applications. Therefore, it is important to deposit boron doped epitaxial layers with low defect density for electrochemical applications. Diamond epitaxial layers with lowest density of defects and highest electrical properties [3] are obtained on crystal with (100) orientation. Thin atomically flat and device grade epitaxial diamond layers have been obtained by microwave plasma enhanced chemical vapour deposition (MW PE CVD) at low CH_4/H_2 ratio (<0.05%) on (100) oriented substrates of [4, 5]. Nonetheless, G. Bogdan et al. also reported deposition of thick, near-atomically flat and intrinsic epitaxial layers at high methane concentrations and relatively high deposition rate [6]. The objective of this work is to optimise the epitaxial diamond growth process to obtain boron doped layer with flat and defects free surfaces at high deposition rate.

2. EXPERIMENTAL

Boron doped diamond epitaxial layers were grown in a 1.5 kW resonance cavity microwave plasma enhanced chemical vapour deposition system AX5010 from Seki Diamond Systems equipped with UHV pumping unit. The base pressure of the system is below 2×10^{-6} mbar. Substrates in this work are 3×3 mm^2 synthetic high pressure high temperature Ib Sumicrystal UP from Sumitomo Electrics Hartmetall GmbH [7]. First, diamond substrates are cleaned in oxidizing mixture of hot sulphuric acid (H_2SO_4) and potassium

nitrate (KNO_3) for 10 minutes. After this acid cleaning, diamond substrates are washed in hot deionized water in ultrasonic bath and air dried. Prior epitaxial growth diamond substrates were plasma etched in hydrogen oxygen mixture in the AX 5010 deposition system. After etching, doped diamond layers are grown in a mixture of 1% of methane (5.4) diluted in hydrogen (6.0) at a total pressure of 110 mbar for a total flow rate of 500 sccm, a microwave power of 550 W and a substrate temperature of 1000-1100 °C. Boron doping is achieved using trimethylboron (TMB) diluted in hydrogen (2000 ppm). The temperature was measured using a double wavelength pyrometer from Williamson model PRO 92-38. The deposition rate of 3.7 µm/h was calculated from double mass measurement of samples using a high precision ME5 microbalance (Sartorius).

After deposition, the surface morphology of sample was observed by optical microscopy, atomic force microscopy (AFM) in semi contact mode using INTEGRA-Prima a microscope and by a Zygo NEWVIEW 7200 white light profilometer. Preliminary electrical properties measurement were carried out by Hall effect measurements using a commercial Accent HL 5500PC Hall effect measurement setup equipped with a cryostat operating between 100 K and 500 K. Before electrical measurements, samples were oxidized in hot sulphuric acid mixed with potassium nitrate and rinsed in DI water. Titanium gold ohmic contacts were deposited by evaporation technique using an Edwards Auto 500 Vacuum Coating System and annealed in vacuum at 450°C during 30 minutes. Finally, Doped epitaxial diamond layers have been also characterized by standard confocal Raman spectrometry at room temperature using an Ar-laser excitation line (514.5 nm).

3. RESULTS AND DISCUSSIONS

A series of boron doped epitaxial layers has been grown on (100) oriented Sumicrystal UP from Sumitomo Electric Hartmetall GmbH with various boron precursor gas concentrations. The carbon to boron ratio in the gas phase was varied from 50 to 4000 ppm. **Fig. 1** shows the typical surface morphology of these layers observed by optical microscopy. The surface is densely covered with four-fold symmetry hillocks and several non-epitaxial grains can be observed. In addition, hillocks' density seems to increase with TBM concentration. One can also see on several places that hillocks are aligned with polishing lines. Hillocks growth is well known issue on (001) epitaxial CVD diamond layers. Their formation is attributed from nucleation at surface defects (penetration twins or dislocations) or repeated two-dimensional nucleation [8]. Surface's steps and kinks are energetically most favourable sites for nucleation and growth. Surface morphology of substrates has been checked by optical microscopy and profilometry (see **Fig. 1**). Measured surface root mean square roughness is high: R_{RMS} ~ 4 nm and average roughness (R_a) as high as 13 nm. Polishing lines, that are potential nucleation sites for hillocks' growth, are clearly visible using both observation techniques.

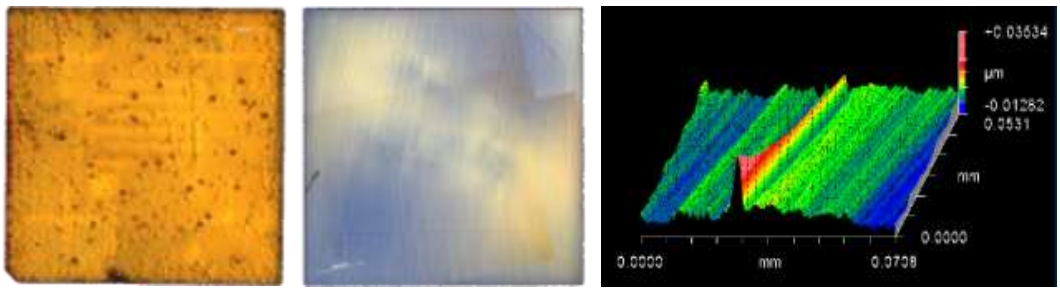

Fig. 1 Optical microscopy picture of a boron doped diamond layer grown on a (100) oriented single crystal with a [TMB]/[CH_4] ratio of 500 ppm (left); Optical microscopy picture of as received Sumicrystal UP from Sumitomo Electric Hartmetall GmbH (middle); surface morphology measured by optical profiler (right).

In order to reduce the density of hillocks, two surface treatments of the substrates have been tested: plasma etching and higher quality polishing, to remove surface defects and to reduce surface roughness. Plasma etching were carried out in the following conditions: 2% oxygen in hydrogen, 100 mbar pressure and 500 W

microwave power. A multi-step etching has been carried out to determine etching rate and to observe the evolution of the surface morphology. The etching rate measured by sample mass variation is 3.7 μm/h. **Fig. 2** shows the substrate's surface morphology etched for 3 hours. The surface is covered by squared etch pits and on several places, large and deep pits (several micrometres) are observed (black spots on optical microscopy image). **Fig. 3** shows the surface morphology of the boron doped diamond layer grown on this substrate. Its surface is free of non-epitaxial grains but it is paved by squared with edges parallel to <110> directions and *truncated at the top* hillocks of few 100s micrometres wide and few 100s nanometres height (~500 nm). Another boron doped diamond layer has been grown on a Sumicrystal UP that has been etched during a shorter time (1 hour). The etching step reveals clearly polishing lines and other surface defects created during polishing. Surface morphology of deposited layer is smoother (R_{RMS}=13 nm) without non-epitaxial grains. Small hillocks are observed mainly on polishing lines (**Fig. 4**).

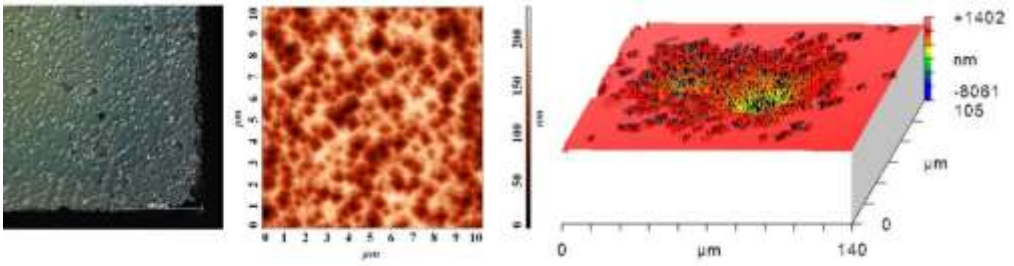

Fig. 2 Optical microscopy pictures and (middle) AFM pictures of Ib (100) oriented single crystal after O_2-H_2 plasma etching (left). Surface profile large pits formed during plasma etching measured using optical profiler (right).

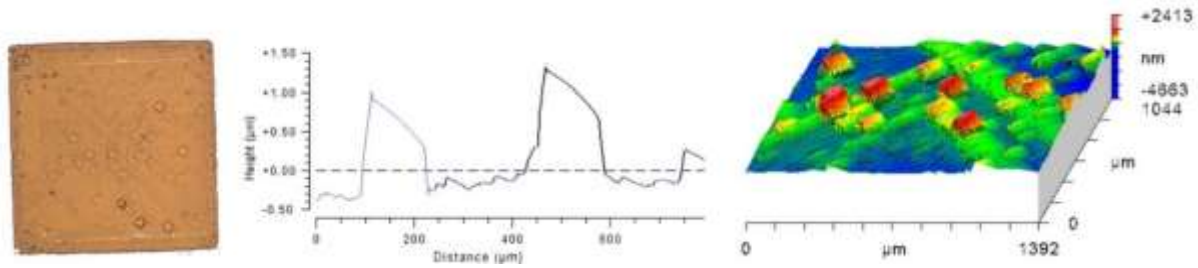

Fig. 3 Optical microscopy picture of a boron doped diamond (1000 ppm) layer grown on 7 hours etched (100) oriented single crystal (left); 1D (middle) and 3D (right) surface profile of boron doped diamond layer's surface measured by optical profiler.

Fig. 4 Comparison the morphology measured by optical microscopy of etched (left), and grown surfaces (right).

Polishing was made using scaife's technique which is used within the gem trade to fashion rough diamonds into cut stones (e.g. round brilliants). First, 10 μm have been removed by polishing to get rid of any damages caused by the previous polishing process. Substrates were polished on the soft polishing direction to

minimise any sub surface damages to produce a smooth surface R_{RMS} <1 nm. Measured surface root mean square roughness after polishing is 0.8 nm and average roughness (R_a) as high as 0.5 nm. No polishing lines are visible under optical microscope. Prior the boron doped diamond epitaxial layer, the substrate were also plasma etched for one hour. Epitaxial layers grown for one hour are very smooth and quasi free of surface defects. The surface morphology was further characterized by atomic force microscopy. The surface is smooth with root mean square roughness of ~ 1 nm and consists of atomic steps (**Fig. 5**). Additionally, 35 μm thick boron doped epitaxial diamond layers have been grown. Despite the presence of few large truncated hillocks, their surface is very smooth on relatively large area (100 x 100 μm) and could not be resolved with AFM (R_{RMS} < 0.1 nm) for the best samples.

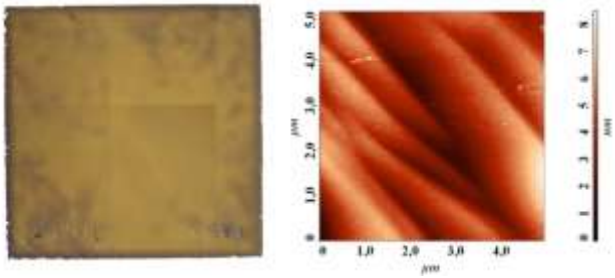

Fig. 5 Optical microscopy image (left) and atomic force microscopy image (right) of boron doped epitaxial diamond layer (1000 ppm) deposited on re-polished sample and etched substrate.

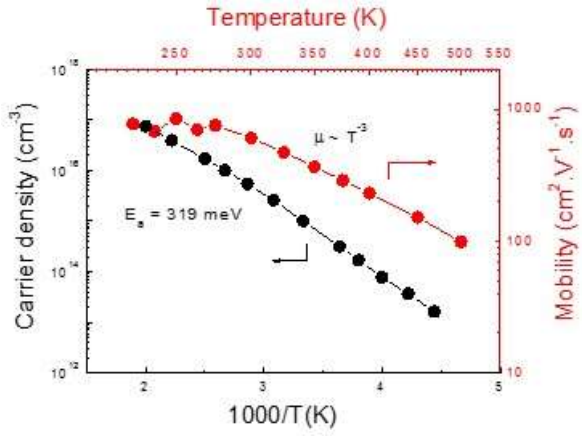

Fig. 6 Arrhenius plot *of carrier concentration and log-log plot of Hall mobility as a function of temperature of not intentionally boron doped diamond layers.*

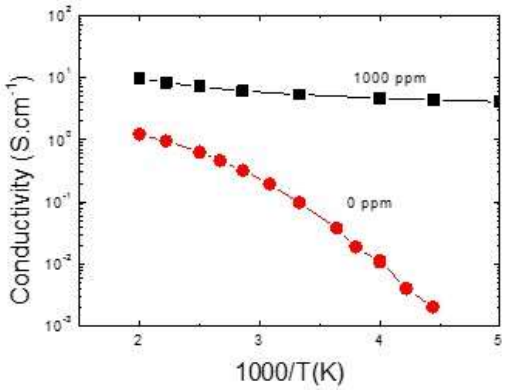

Fig. 7 Arrhenius plot of conductivity of not intentionally boron doped diamond layers and doped (1000 ppm) boron doped diamond layers.

Samples grown on substrates treated by the above high-quality polishing, grown either with no TMB addition or with addition on 1000 ppm of TMB in gas phase, have been characterized using the van der Pauw method. **Fig. 6** shows the temperature dependence of carrier density and mobility of the not intentionally doped sample. The linear variation of the carrier concentration in the Arhrenius plot allows the determination of the activation energy. The activation energy E_a = 319 meV is closed to the thermal ionization energy of boron acceptor in diamond (373 meV). As Hall measurement at higher temperature (up to 900-1000K) is required for the determination of active boron concentration and compensation, the boron concentration has been estimated to be 10^{18} cm^{-3} from carrier concentration at room temperature. This indicates the high boron background of the reactor. Carrier mobility varies from 850 to 100 $cm^2.V^{-1}.s^{-1}$ as temperature increases from 225 to 500 K in a power function ($\mu = T^{\alpha}$) with an alpha parameter of -3. This behaviour is characteristic of

phonons at high temperatures. **Fig. 7** compare the conductivity of not intentionally doped diamond layer to boron doped diamond layer (1000 ppm in the gas phase). The conductivity of the doped diamond is weakly temperature dependent as well as its carrier density (10^{19} cm^{-3}) and mobility (4 $cm^2.V^{-1}.s^{-1}$).

4. RESULTS AND DISCUSSIONS

Boron doped diamond layers have been grown by microwave plasma enhanced chemical vapour deposition system with various B/C ratios in the gas phase. Effect of surface polishing and O_2/H_2 plasma etching on type Ib (100) HPHT synthetic diamonds on surface morphology of epitaxial doped diamond layer has been investigated. Using optimized substrate preparation, i.e. substrate polishing and short O_2/H_2 etching, smooth (R_{RMS} ~ 1 nm) boron doped diamond layers and free of none epitaxial crystallites have been grown with a relatively high growth rate of 3.7 μm/h. Semiconducting p-type diamond layers with mobility of 600 $cm^2.V^{-1}.s^{-1}$ at room temperature and estimated active boron concentration of 10^{18} cm^{-3} have been obtained as well as layers with high conductivity ~ 6 $S.cm^{-1}$.

ACKNOWLEDGMENT

Special thanks to the Analytical Laboratory team from Institute of Organic Chemistry and Biochemistry AS CR, v.v.i. for mass measurements; and to Ivan Gregora for support with Raman spectroscopy, to Václav Petrák and Marie Jakl Krečmarová for their contribution of this work from the Institute of Physics AS CR, v.v.i. Financial support from the Academy of Sciences of the Czech Republic, Czech Science Foundation (GACR) Grant ID: GAČR 13-31783S. J.E. Purkyne fellowship awarded to Vincent Mortet by Academy of Sciences of the Czech Republic.

REFERENCE

[1] FUJISHIMA, A., EINAGA, Y., RAO, T. N., TRYK, D. A. *Diamond Electrochemistry*, Elsevier, Tokyo, 2005.

[2] LUONG, J. H. T., MALE, K. B., GLENNON, J. D. *Boron-doped diamond electrode: synthesis, characterization, functionalization and analytical applications*, Analyst 134 (2009) 1965.

[3] MORTET, V., DAENEN, M., LAZEA, A., D'HAEN, J., HAENEN, K., D'OLIESLAEGER, M. *Characterization of boron doped diamond epilayers grown in a NIRIM type reactor*. Diam. Rel. Mat. 17 (2008) 1330.

[4] OKUSHI, H. Diam. Relat. Mater. 10 (2001) 281.

[5] TAKEUCHI, D., WATANABEA, H., YAMANAKAA, S. OKUSHIA, H., KAJIMURA, K. *Homoepitaxial diamond films grown by step-flow mode in various misorientation angles of diamond substrates.* Diam. Relat. Mater. 9 (2000) 231-235.

[6] BOGDAN G., NESLÁDEK, M., D'HAEN, J., MAES, J., MOSHCHALKOV, V. V., HAENEN, K. AND D'OLIESLAEGER, M. *Growth and characterization of near-atomically flat, thick homoepitaxial CVD diamond films*, phys. stat. sol. (a) 202 (2005) 2066.

[7] Sumitomo Electric Hardmetal Corporation. [online]. [cit. 2014-09-30]. Available at: http:/www.sumitool.com.

[8] LEE, N., BADZIAN, A. A study on surface morphologies of (001) homoepitaxial diamond films. Diam. Relat. Mater. 6 (1997) 130.