OPTIMIZATION AND CHARACTERIZATION OF POROUS BORON DOPED DIAMOND LAYERS

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Abstract

With the development of chemical vapour deposition techniques, and thanks to its chemical and electrical properties, boron-doped nanocrystalline diamond has attracted the interest of electrochemists for various applications from chemical sensing to water treatment. Potential applications, such as super capacitors and dye sensitized solar cells, would greatly benefit from an increase in specific surface area. We recently reported a promising simple multilayer process using SiO_2 nanofibres as a 3D template to produce thick porous boron doped diamond (PBDD). In this article, we further describe the optimization and characterization of thick PBDD layers: addressing diamond seeding issues and report on electrical conductivity and electrochemical properties. Fabricated PBDD layers were characterized by scanning electron microscopy, micro-Raman spectroscopy, and cyclic voltammetry in aqueous electrolyte solution. Finally, fabrication of thick free-standing PBDD layer is demonstrated.

Keywords: Porous materials, boron doped diamond, electrochemistry, nanofibres, MW PECVD

1. INTRODUCTION

Progressive electrochemical technologies, such as dye-sensitized solar cells, supercapacitors, electro-analysis or water treatment, require the use of high quality material as electrodes for highly effective and long service life time. Due to its excellent properties, such as a large potential window in aqueous media, high corrosion resistance as well as low background current, boron doped diamond is of particular interest for these applications. The performance of boron doped diamond electrodes can be potentially significantly increased by enlargement of its specific surface area. Various top-down etching [1, 2] or bottom-up growth [3-5] methods to enlarge the ratio of the specific surface area to the geometric electrode area have been studied. We recently reported an alternative simple multilayer MW PECVD bottom-up PECVD growth process to produce stable porous diamond electrodes based on a SiO_2 nanofibres/polymer mix method [3]. In contrary to top-down etching methods with limited aspect ratio [5], this novel method is not limited in thickness. In this work, we report on the optimization of the fabrication process of porous boron doped diamond (PBDD) using a nanofibres/polymer mix method to address the problem of non-reproducible diamond seeding, and report on characterization the fabricated layers' structural, electrical and electrochemical properties.

2. EXPERIMENTAL

PBDD layers were obtained by consecutive diamond depositions on a thin SiO_2 nanofibre template (electrospun SiO_2 nanofibres produced by Elmarco, Ltd., Czech Republic). The porous template was prepared by deposition of a SiO_2 nanofibre/photoresist mix by spin coating at 3000 rpm for 30s. Boron doped diamond was deposited using an ASTeX 5010 microwave plasma enhanced chemical vapour deposition (MW PECVD) reactor with 0.5 % methane in hydrogen, at 50 mBar, and a microwave power of 1150 W and a deposition temperature of c.a. 720 °C and a deposition rate of c.a. 250 nm/h. Boron doping was realized by addition of trimethylborane in the gas phase with a B/C concentration of 2000 ppm. Morphology and quality of fabricated PBDD layers were evaluated by scanning electron microscopy using a FERA 3 (TESCAN) and Raman spectroscopy using a Renishaw inVia Raman microscope with 488 nm excitation wavelength. Sheet resistance of fabricated PBDD layers was determined using van der Pauw measurement method. Electrical contacts were obtained by deposition of four carbon paste drops on the four corners of the layer deposited on fused silica substrate. PBDD layers were also characterized by cyclic voltammetry (CV) performed in an aqueous phosphate buffer solution with pH 7 (PBS, Sigma Aldrich) at a scan rate of 100 $mV{\cdot}s^{-1}$ using a three electrode closed cell under argon atmosphere. The porous BDD were used as a working electrode, a platinum mesh was a counter electrode and Ag/AgCl electrode (sat. KCl) was a reference. Electrochemical experiments were carried out using AUTOLAB PGSTAT128N potentiostat (Metrohm) controlled by GPES4 software. The specific surface area, i.e. surface roughness factor, was determined from cyclic voltammetry measurements as well as by Kr adsorption isotherms (BET).

3. RESULTS AND DISCUSSION

3.1. Nanofibres/polymer mix optimization

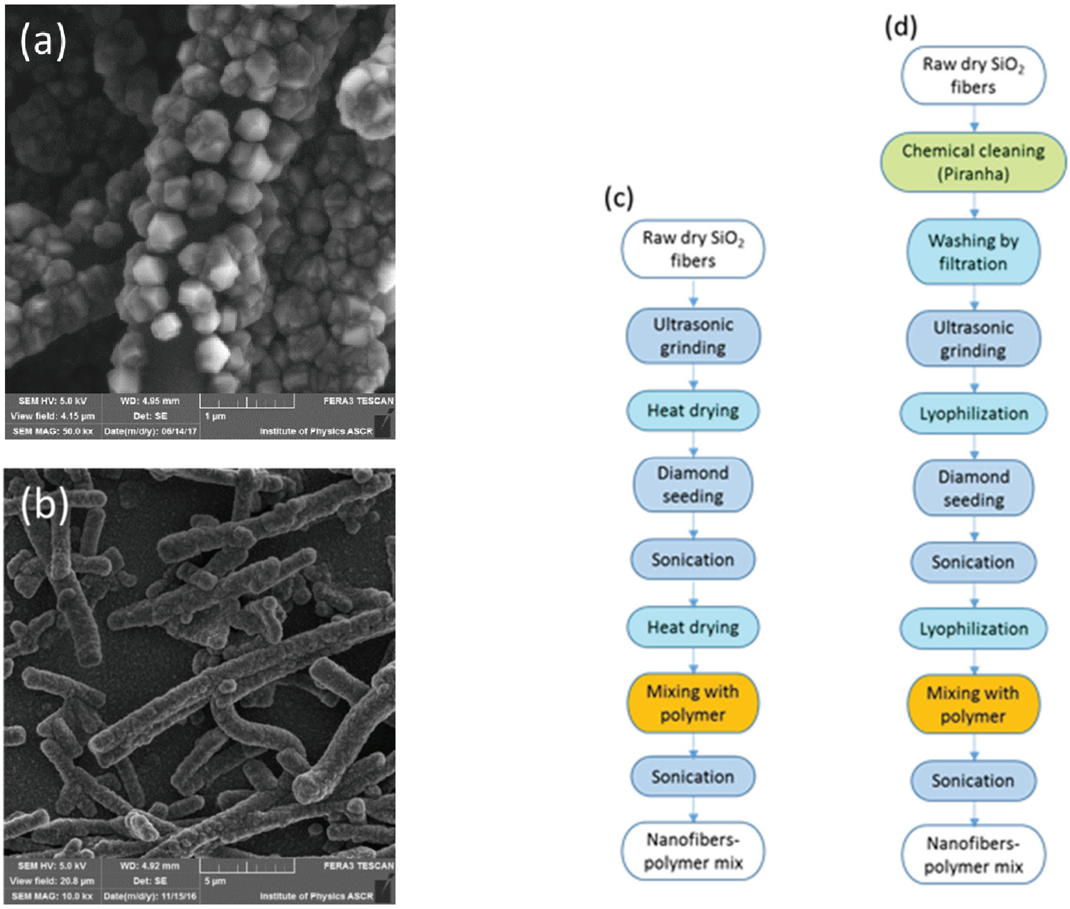

Figure 1 SEM image of (a) diamond coated SiO_2 nanofibres with inhomogeneous seeding and incomplete diamond coverage (b) homogeneous seeding and complete diamond coverage; Original (c) and optimized (d) process flow for the preparation of SiO_2 nanofibres/polymer mix

The initial preparation of the nanofibres/polymer mix as described in Ref. [6] suffered from inhomogeneous diamond seeding and following growth, incomplete diamond coverage of the SiO_2 nanofibres (**Figure 1 (a)**). In order to resolve these issues, we studied the effect of alternative processing methods of the numerous preparation steps of the polymer mix, i.e. chopping, seeding, drying, and mixing of the SiO_2 fibres. **Figure 1** compares the original preparation process (c) with the newly optimized process (d) of the nanofibres/polymer mix preparation. Cleaning of the raw SiO_2 fibres in Piranha solution, mixture of H_2SO_4:H_2O_2 (3:1), for 20 min. is the first implemented step. The Piranha solution removes organic impurities and increases hydrophilicity in order to improve diamond nucleation. The fibres were then rinsed in DI water and filtered several times until the remnant solution reached a neutral pH. After cleaning, fibres were chopped in DI water and sonicated using an UP400S Ultrasonic processor Hielscher for 10 mins (parameters: 400 W, 10 min., duty cycle 50%). In contrary to the previous recipe, chopped fibres were dried by lyophilization instead of evaporation. Lyophilization prevents aggregation of fibres which was observed during the evaporation drying method and also eases the dispersion in the seeding solution and photoresist. Dried SiO_2 fibres were next mixed and sonicated (400 W, duty cycle 50%) for 10 min. with a nano-diamond seeding solution (NanoAmando®B - aqueous colloid of 0.2 $g.l^{-1}$ concentration) using per each 50 mg of fibres/ 1.5 ml of nano-diamond seeding solution. Finally, the optimized sonicated mixture of seeded and lyophilized SiO_2 fibres was added to ma-P 1210 photoresist (Microresist Technology) to obtain concentration of c.a. 80 $mg.ml^{-1}$. This method demonstrated excellent diamond seeding and diamond coverage (see **Figure 1 (b)**) as well as long storage life time with over 6 months stability.

3.2. Porous layers fabrication and characterization

Thick PBDD layers were obtained by consecutive MW PECVD diamond deposition of spin-coated SiO_2 fibres/photoresist mixtures. The spin-coated deposited c.a. 4-5 μm thick layer of SiO_2 fibres/photoresist mix was baked at 110 °C on a hot plate for 90 s. The SiO_2 fibres within the deposited mixture serve as a porous 3D template for diamond deposition. Due to the effects of high deposition temperature (c.a. 720 °C) and the hydrogen plasma, the photoresist is decomposed allowing the diamond coating of the SiO_2 fibres. In this work, porous layers with up to 10 consecutive diamond coatings have been prepared on 10×10 mm^2 silicon and fused silica substrates. The surface morphology and the thickness homogeneity of the porous SiO_2 and doped diamond composite are shown in **Figure 2**.

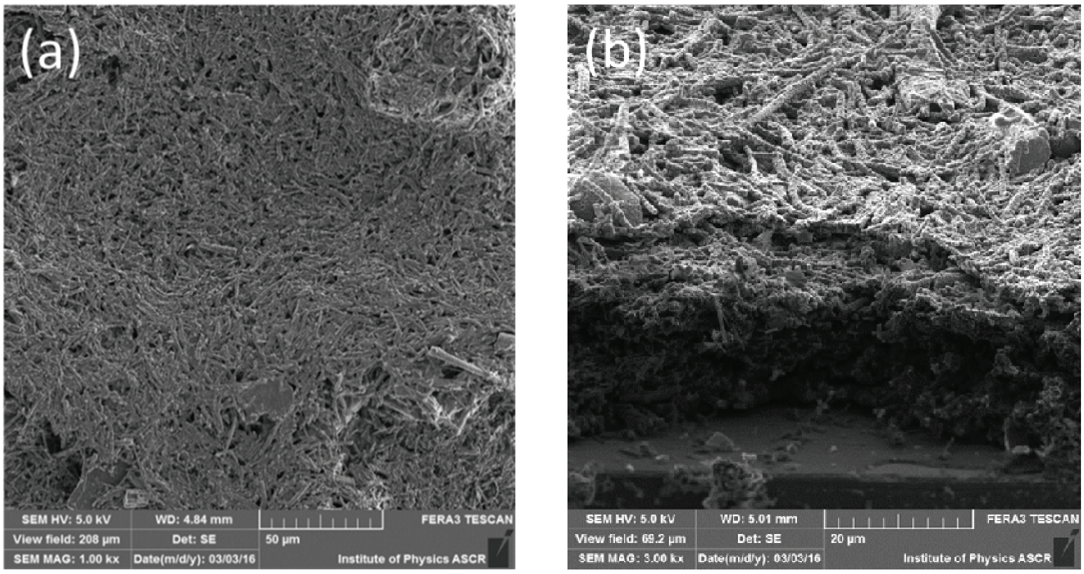

Figure 2 (a) Surface and (b) cross-section scanning electron microscopy pictures of a 26 μm thick diamond layer obtained by 6 consecutive PECVD diamond coatings

Figure 3 (a) shows a thicker PBDD layer structure obtained by 10 consecutive MW PECVD diamond coatings on a 30×30 mm^2 silicon substrate. The layered structure has been successfully removed from its silicon substrate by wet chemical etching in HF and HNO_3 and laser cut to various desired shapes (**Figure 3 (b)**).

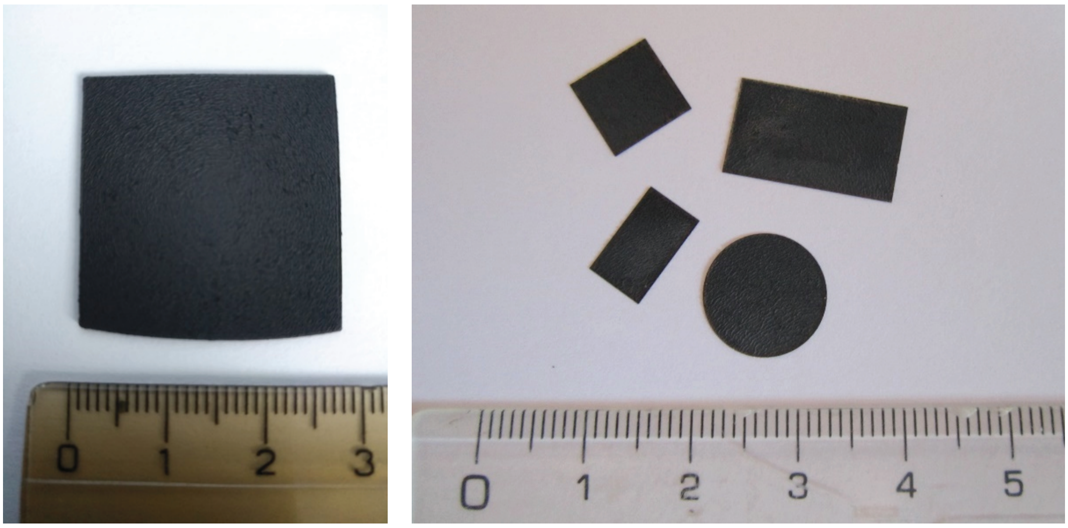

Figure 3 (a) Thick (c.a. 45 μm) porous boron doped diamond layer deposited on a 30 × 30 mm^2 silicon substrate obtained by 10 consecutive MW PECVD diamond coatings. (b) Thick free-standing porous boron doped diamond layer (c.a. 45 μm) laser cut with various desired shapes obtained after removal of the Si substrate via wet chemical etching in hydrofluoric acid and nitric acid.

Figure 4 (a) shows the evolution of the PBDD thickness as a function of the consecutive deposition steps. The thickness increases by c.a. 4.4 μm after each nanofibres/ polymer mix and PECVD diamond deposition. **Figure 4 (b)** shows the evolution of the sheet resistance of the PBDD layer deposited on a fused silica substrate as a function of the thickness of MW PECVD stages on the nanofibres/polymer mix. These results are compared to the sheet resistance of a boron porous doped diamond layer. The sheet resistance is inversely proportional to the PBDD layer thickness, which corresponds to a resistivity of c.a. 136 mΩ.cm^{-1}.

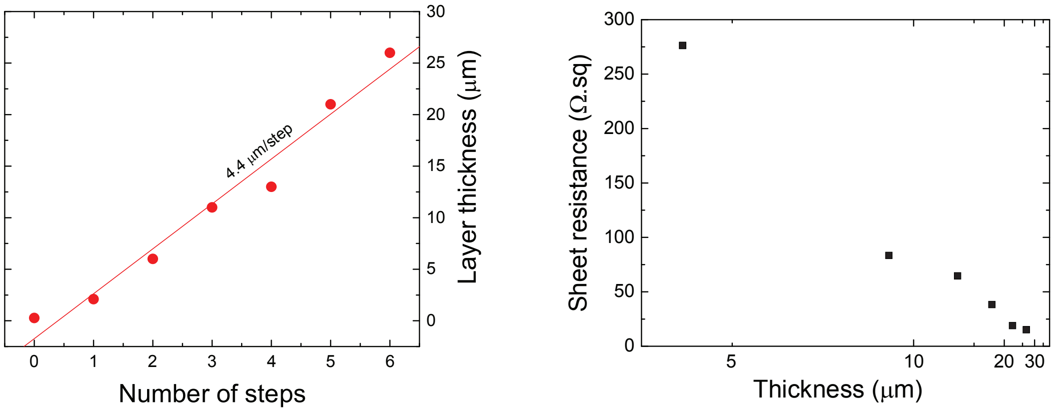

Figure 4 (a) Variation of thickness of PBDD layers as function of the number of consecutive depositions of the polymer mix and MW PECVD growth stages; (b) Variation of the sheet resistance versus reciprocal PBDD layer

Raman spectra of as deposited diamond layer (**Figure 5 (a)**) exhibits the characteristic peaks of heavily boron doped diamond: the red-shifted diamond peak, the c.a. 1200 cm^{-1} and c.a. 500 cm^{-1} peaks [7]. Superimposed to these characteristic peaks are observed non-diamond (sp^2) carbon D- and G-peaks present at c.a. 1340 cm^{-1} and c.a. 1587 cm^{-1} as well as the two peaks centred at c.a. 1150 cm^{-1} and 1450 cm^{-1} assigned to trans-polyacetylene. Following wet chemical oxidation (hot H_2SO_4 and KNO_3), in order to remove co-deposited non-diamond carbon impurities, the intensity of their respective peaks is reduced.

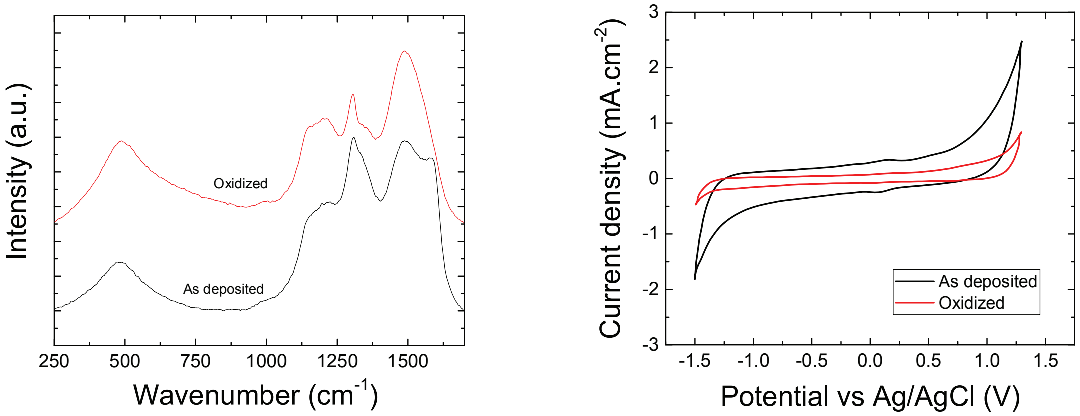

Figure 5 (a) Comparison of Raman spectrum of as deposited and oxidized thick PBDD layer (x6 PBDD layers); (b) Comparison of as deposited and oxidized thick PBDD layer cyclic voltammograms

Figure 5 (b) compares the cyclic voltammograms of as deposited (black line) and oxidized (red line) 26 µm thick porous boron doped diamond layer. The background currents drops by a factor of 4 and the potential window increases from c.a. 1.5 V to c.a. 2.5 V vs. Ag/AgCl reference electrode after wet oxidation, i.e removal of non-diamond carbon. The voltammetric double layer capacitance of as deposited porous BDD related to the projected geometric (2D) surface area is 2.5 mF.cm^{-2} (roughness factor ca. 830), whereas normalized to the BET surface area determined by krypton adsorption isotherms the capacitance is significantly lower, i.e. 57 µF.cm^{-2}cm2 (roughness factor 44). The double layer capacitance of the same porous BDD after oxidative treatment decrease to the value of 0.6 mF.cm^{-2}cm2 (geometric surface area) clearly evidencing the important contribution of the faradaic pseudocapacitance of the surface oxides interconnected with sp^2 impurities, which are removed during wet oxidation [8].

4. CONCLUSION

In summary, the preparation of the SiO_2 nanofibres/polymer mix has been improved by Piranha cleaning and lyophilization steps instead of heat drying to improve diamond seeding and diamond coverage. Porous boron doped diamond layers with various thicknesses, up to c.a. 40 µm, have been fabricated and characterized by Raman spectroscopy, scanning electron microscopy, Van der Pauw and cyclic voltammetry methods. PBDD layers show an electrical resistivity of 136 mΩ.cm^{-1}. After wet chemical cleaning, fabricated layers exhibit good electrochemical properties as measured by cyclic voltammetry. Finally, fabrication of free-standing boron doped porous diamond layers has been demonstrated.

ACKNOWLEDGEMENTS

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