Optically transparent boron-doped nanocrystalline diamond films for spectroelectrochemical measurements on different substrates

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Abstract. Fabrication process of optically transparent boron nanocrystalline diamond (B-NCD) electrode on silicon and quartz substrate was shown. The B-NCD films were deposited on the substrates using Microwave Plasma Assisted Chemical Vapor Deposition (MWPACVD) at glass substrate temperature of 475 °C. A homogenous, continuous and polycrystalline surface morphology with high sp³ content in B-NCD films and film thickness depending from substrate in the range of 60-300 nm was obtained. The high refraction index and transparency in visible (VIS) wavelength range was achieved. Moreover, cyclic voltammograms (CV) were recorded to determine reaction reversibility at the B-NCD electrode. CV measurements in aqueous media consisting of 1 mM K₃[Fe(CN)₆] in 0.5 M Na₂SO₄ demonstrated relatively fast kinetics expressed by a redox peak splitting below 503 mV for B-NCD/silicon and 110 mv for B-NCD/quartz.

1. Introduction
Nanocrystalline diamond (NCD) film, which exhibit outstanding properties such as: hardness, chemical resistance, biocompatibility [1,2] and so on, also have optical transparency in a broad wavelength range from ultraviolet (UV) to far infrared (IR). Natural diamond is a wide-band semiconductor $E_g = 5.45$ eV that can be easily doped by boron atoms using the in situ Microwave Plasma Assisted Chemical Vapour Deposition (MWPACVD) process. Due to this properties, boron-doped diamond films are promising materials for optically transparent electrodes that have various applications, e.g. spectroelectrochemical measurements. Fused silica substrates allow working in wavelength range from 160 to 4000 nm and are resistant to hazardous media. Silicon substrates not only allow working in the IR wavelength range but also are optimal material for planar waveguides, resonators etc. The optical transparency of the MWPACVD polycrystalline diamond are strongly influenced by surface roughness, boron doping film thickness or nondiamond phases and other impurities.
Boron-doped diamond films are commonly used as materials for electrodes for sensing various organic substances or as electrodes to utilization hazardous organic compounds like phenolons, etc. Hence, they are promising materials for developing sensors based on optically transparent electrodes or as protective coatings for biomedical applications [3], due to optical transparency and biocompatibility. Zak et al. [4] proposed boron-doped diamond as an optically transparent electrode material. The authors reported a 0.38 mm thick freestanding electrode for spectroeletrochemical measurements. Stotter et al. [5,6] applied boron-doped diamond electrodes to spectroeletrochemical studies in the UV-VIS wavelength region showing good transparency at 50–60%.

The present paper reports thin and continuous optically transparent and conducting boron-doped nanocrystalline diamond (B-NCD) films on quartz and silicon substrates using a MWPACVD. To achieve good quality of optical and conducting properties, optimization of growth parameters is needed. The usage of a truncated cone-shaped substrate holder [7] enables an increase of microwave power density, yielding a high sp$^3$/sp$^2$ ratio, small roughness, lower growth rate, and more effective boron incorporation to diamond lattice [8].

The thin B-NCD film were performed by MWPACVD. The film morphology was investigated by numerical analysis of scanning electron microscopy (SEM). The chemical composition of the films was investigated by means of Raman spectroscopy. The thickness and optical properties in the UV-VIS wavelength range were estimated using spectroscopic ellipsometry (SE). Electrochemical measurements e.g. cyclic voltammetry and chronoamperometry were used to investigated redox reaction reversibility at the electrode and to carry out spectroelectrochemical measurement.

2. Experimental

2.1. A CVD nanocrystalline diamond film deposition

B-NCD films were synthetized in an MWPACVD system (SEKI Technetron AX5400S, Japan) on optically polished quartz and single-crystal p-type Si (100) substrates. The substrates were seeded by means of spin-coating, spun three times by 60 seconds with 4000 rpm, using nanodiamond DMSO/PVA base slurry with crystallites size 4-7 nm. The substrate temperature was maintained at 475 °C during the deposition process. A special truncated cone-shaped shim was used during the growth of diamond films. Excited plasma was ignited by microwave radiation (2.45 GHz) [9]. The plasma microwave power, optimized for diamond synthesis, was kept at 1300 W. In this study, the molar ratio of CH$_4$-H$_2$ mixture was kept at 1% of gas volume, whose total flow rate was set at 300 sccm. The base pressure was about 10$^{-6}$ Torr (10$^{-4}$ Pa) and the process pressure was kept at 50 Torr (6.6 kPa). The boron level expressed as the [B]/[C] ratio in the gas phase was 0, 2000, 5000, 7500 or 10,000 ppm. Diborane (B$_2$H$_6$) was used as a dopant precursor. The mirror polished substrates were covered by B-NCD film, essentially providing full surface encapsulation. The growth time was 1 hour for Si substrates and 3 hours for quartz.

2.2. Electrochemical and spectroelectrochemical setup

Cyclic voltammetry (CV) measurements were carried out in aqueous media consisting of 5 mM K$_3$[Fe(CN)$_6$] in 0.5 M Na$_2$SO$_4$ at a scan rate of 100 mV s$^{-1}$. Electrochemical cell consisted of a three electrode system. B-NCD, platinum wire and Ag/AgCl/0.1 KCl were used as working, counter and reference electrodes, respectively. The area of the working electrode exposed to electrolyte was 0.5 cm$^2$. The electrochemical experiment was performed using an Autolab potentiostat/galvanostat (PGSTAT30 and GPES 4.9 software/Nova 1.10.2, Netherlands). The spectroelectrochemical measurements were carried out in thin-layer electrochemical cell consisting 30 µL of solution.
2.3. Surface and structure analytical techniques

A scanning electron microscope (S-3400 N, Hitachi, Japan) with a tungsten source and variable chamber pressure (VP-SEM) was utilized to inspect the surface of synthesized thin films. The molecular composition of films was studied by means of Raman spectroscopy using a Raman confocal microscope (Horiba LabRAM ARAMIS, Japan). Spectra were recorded in a range of diode pumped solid state (DPSS) laser in combination with a 100x objective magnification (NA = 0.95) and 50 lm confocal aperture.

The ellipsometric parameters Ψ, Δ and depolarization factor (%Depol) were measured for three angles of incidence (65°, 70°, 75°) in range from (300 - 1000 nm) with a step of 0.02 eV at the room temperature of 20 °C by means of a rotating analyser device (V-VASE, J.A. Woollam Co. Inc, USA (196 – 2200 nm).

A five-layer structural model of the samples (ambient / SRL- surface roughness layer / B-NCD / intermix / Si – substrate) was applied to determine the effective thickness (d) of the SRL and the thickness of the B-NCD film (dl) and its effective complex dielectric function , where ε1, ε2 and are the real part, the imaginary part of and the effective complex refraction index, respectively. The thickness of the intermix layer [10] had been derived in a previous investigation and was set as di~2 nm for all samples in this study. Optical responses of roughness and intermix layers were estimated using Bruggeman effective medium approximation (EMA). The optical response of a B-NCD film was predicted using the sum of Drude and Lorentzian oscillators. Generally, a semi-classical form of the complex effective dielectric function can be written as [11]:

$$\langle \varepsilon \rangle = \varepsilon_{\infty} - \frac{\left(\hbar \omega_p^2\right)^2}{E^2 + i\Gamma E} + \sum_k \frac{A_k E_{0k}^2}{E_{0k}^2 - E^2 - i\gamma_k E}$$

In Eq. (1) ε∞, ωp and Γ define the high-frequency dielectric constant, the unscreened plasma frequency and the free-carrier damping, respectively. The inter-band transitions are represented by the Lorentz oscillator located at photon energy E_{0k} with amplitude A_k and broadening parameter γ_k. In this study, a single Lorentzian oscillator was used to characterize the UV-VIS absorption.

3. Result and discussion

3.1. Surface morphology and chemical composition of B-NCD films

Fully investigation of B-NCD/silicon samples is described in our previous paper [9]. SEM surface investigation shows fully encapsulation on both substrates without any cracks, defects or impurities. The average grain size achieved for silicon were below 100 nm due to 1 hour of deposition. Figure 1 shows high resolution SEM micrographs for B-NCD/quartz sample with boron doping at 5000 ppm level.
Figure 1. SEM micrographs of 10000x and 50000x magnitude for 5000 ppm B-NCD film on quartz substrate.

It can been see that diamond film is continuous and uniform with grain size in range from 50 up to 250 nm and should be notice that time of deposition is 3 hours. In case of quartz substrates shorter time of diamond film deposition occurs with cracks that are connected with internal stress deriving from difference of thermal expansion coefficient between quartz and diamond. Moreover film cracking have minor impact on optical properties but significant on electrical parameters.

Raman spectrum for B-NCD/quartz samples shown in Figure 2 proves presence of strong bands assigned to the diamond lattice, and confirms high content of sp³ carbon in the film structure. Its shift from typical for diamond 1332 to about 1305 cm⁻¹ with boron doping increasing and is caused by a stress introduced by boron atoms [12]. Moreover, the boron presence in sample B-NCD-10 (10000 ppm [B]/[C]) can be confirmed by a band at 1211 cm⁻¹ and strong signal intensity drop above 1650 cm⁻¹. The peaks at band 1131 to 1148 can be assigned as nanocrystalline diamond or tetrahedral amorphous carbon (ta-C) with about 90% sp³ bonding [13–15]. The D band at 1474 to 1478 cm⁻¹ can be assigned to the mixture of amorphous carbon phase sp² and sp³, while the G band at 1537 to 1555 cm⁻¹, to sp²-bonded amorphous carbon.
3.2. Optical properties of boron nanocrystalline diamond

The refraction index) $n$ is a crucial parameter in design of various kinds of waveguides, sensors, coatings etc. It is also important in coupling different materials. Since $n$ is correlated with the materials density [16,17], a high refractive index determines a high optical density. Figure 3(a) and 3(b) shows the $n$ for B-NCD/quartz and B-NCD/silicon samples, respectively.

Figure 2. Raman spectra of the ultrathin B-NCD films deposited by MWCVD on quartz substrates, depicting the typical signatures of diamond with different [B]/[C] ratios.
Figure 3. Refractive index of B-NCD samples (a) on quartz and (b) on silicon substrates, insets shows linearity of changing RI with increasing doping for 550 nm.

The obtained values for films on quartz ranged from 2.4 to 1.96 with increasing wavelength. In the case of the non-doped sample, the change of $n$ is minor with increasing $\lambda$ and remains slight for the low doped sample (2000 ppm). For the higher doping level, the impact of changing $\lambda$ on RI is significant. Change of the $n$ at 550 nm with increasing boron doping is linear (Figure 3a inset) with R-square equal to 0.994.
Table 1. The effective thickness and surface roughness of B-NCD/quartz samples.

| [B]/[C] ppm | Thickness nm | Surface roughness nm |
|-------------|--------------|---------------------|
| 0           | 291.79       | 17.04               |
| 2000        | 303.10       | 15.31               |
| 5000        | 272.48       | 10.76               |
| 7500        | 271.72       | 9.12                |
| 10000       | 247.10       | 8.50                |

The boron doping level influences film thickness, which constantly decreases from 303 nm to 247 nm going from 2000 to 10000 ppm samples. Moreover, this is accompanied by a decrease of the surface roughness, yielding half the roughness for 10000 ppm, compared to the undoped sample (see Table 1).

The RI of natural diamond is 2.42 at 550 nm wavelength [18] and B-NCD/silicon film are close to this value for 2000 and 5000 ppm doping. Furthermore, the change of $n$ with increasing wavelength is nearly constant. The significant change of $n$ for 10000 ppm can be explained by the transition of conductivity from semiconducting to semi-metallic/metallic [9]. The refractive index of the 10000 ppm doped sample was similar to that characteristic for metals especially in IR wavelength range [18]. This phenomena can be explained by the high boron content in the diamond film. Boron doping induces an acceptor level at 0.37 eV leading to light absorption for higher energies [19].

Also the change of refractive index, with R square 0.918, is not that linear as in the case of B-NCD/quartz and exhibits a high decrease of $n$ for most doped sample. Hence, the higher values of $n$ for diamond films on silicon substrates indicate a higher density material. The achieved values of RI agree with those found by others groups [20–22].

Figure 4 shows intrinsic transmittance for B-NCD calculated using the determined values of optical constants and thickness and measured transmittance for B-NCD/quartz. All diamond films (B-NCD/silicon) has good transmittance, above 65% for low doped films and 50% for 10000 ppm.

![Figure 4. Calculated transmittance form spectroscopy ellipsometry of B-NCD samples on silicon and measured transmittance for B-NCD/quartz.](image-url)
3.3. Electrochemical and spectroelectrochemical testing

![Figure 5](image)

**Figure 5.** (a) Comparison of CV i-E curves for B-NCD/quartz and B-NCD/silicon for reversibility of redox reaction of 1 mM Fe(CN)$_{6}^{3-/4-}$ in 0.5 M Na$_2$SO$_4$ with a scan rate of 100 mV s$^{-1}$, inset table shows potential and current peaks and $\Delta$E for each i-E curve; (b) recorded spectra of absorbance of 1 mM ferrocyanide (Fe(CN)$_{6}^{4-}$) with different applied potentials.

Cyclic voltammetry (CV) is a very useful and easy method for investigation electrochemical properties of the material interface being with contact with an electrolyte. Fig 5a shows the CV i-E curves for redox reaction of 1mM Fe(CN)$_{6}^{3-/4-}$ in 0.5 M Na$_2$SO$_4$ solution on B-NCD films doped at 5000 ppm level deposited on silicon and quartz substrates, with a scan rate of 100 mV/s. The Fe(CN)$_{6}^{3-/4-}$ redox system is sensitive to surface properties such as $sp^2$ bonded carbon or density of electronic states near the formal potential [23–25]. The redox system undergoes a reversible 1-electron transfer according to the following reaction:

$$Fe(CN)_6^{3-} + e^- \leftrightarrow Fe(CN)_6^{4-}$$

The recorded value of $\Delta$E for B-NCD on silicon is wide and reaches 503 mV and is almost five times higher than those on quartz $\Delta$E = 110 mV, at scan rate 100 mV/s. However, it should be noted that the film thickness strongly influences on electrochemical properties [26]. The B-NCD/quartz shows outstanding electrochemical features combined with good optical transparency and therefore is a promising diamond layer to develop new class of sensors. Moreover, Figure 5b shows a series of spectra recorded during electrochemical oxidation of 1 mM Fe(CN)$_6^{4-}$ in 0.5 M Na$_2$SO$_4$ at potential between 130 and 330 mV that cover the states of solution from the transparent form (130 mV) to fully oxidized form (yellow), which is completely achieved at 330 mV. The process is completely reversible and reproducible showing usefulness of the B-NCD film as optical diamond electrodes in spectroelectrochemistry.

4. Conclusion

In this work we have instigated optical and electrochemical response of optically transparent boron nanocrystalline diamond films on different substrates. The usage of a special sample holder allow achieving good nanocrystalline diamond film with remarkable electrochemical and optical properties. However, it must be emphasized that the working area, grain size and thickness of the B-NCD electrode have a strong influence on carrier transport in the system and optical properties. Application
of electrically conductive B-NCD films allows for developing both optical and electrochemical sensing devices, and, what is more, allows for combining both capabilities in one sensing structure.

5. References
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