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Optical and electrical properties of ultrathin transparent nanocrystalline boron-doped diamond electrodes

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ABSTRACT

The optical properties of ultrathin (less than 100 nm) boron-doped nanocrystalline diamond (B-NCD) film were investigated in a wavelength range of 200–20,000 nm. The B-NCD refractive index showed values close to that of monocrystalline diamond ($n = 2.45$) in a broad wavelength range (450–4000 nm). A transmittance up to 70% and the average film thickness of 70 nm were achieved. A special cone-shaped shim was used in the deposition process. Ultrathin nanocrystalline films were deposited on silicon substrates using the Microwave Plasma Assisted Chemical Vapour Deposition (MW PA CVD) method.

Cyclic voltammetry (CV) measurements in aqueous media consisting of 5 mM $K_3[Fe(CN)_6]$ in 0.1 M Na_2SO_4 demonstrated a width of the electrochemical window up to 2.5 V. The evolution of the surface morphology was analysed using a scanning electron microscope (SEM) and an atomic force microscope (AFM). The chemical composition of B-NCD films was examined with micro-Raman Spectroscopy. The Raman spectra included a diamond peak and a nanocrystalline diamond band at 1330–1333 cm^{-1} and 1126–1143 cm^{-1}, respectively. The thickness and optical properties of ultrathin B-NCD film in UV–MIR wavelength range were investigated using spectroscopic ellipsometry.

1. Introduction

Nanocrystalline diamond (NCD) thin films have focused a great deal of attention due to their outstanding properties, remarkable hardness, optical transparency in a broad wavelength range [1,2], high thermal conductivity [3] as well as biocompatibility [4,5]. Unlike the rough microcrystalline films with grain sizes above 500 nm, NCD films with typical grain sizes less than 100 nm are relatively smooth, showing optical quality and refractive index in the visible wavelength range close to that of single-crystal diamond films [6,7]. Different applications of NCD films have been reported so far, e.g. microelectromechanical systems (MEMS) [8], high power electronics [9], high-frequency devices such as transistors for oscillators [10] or protective coatings for biomedical applications [11]. Diamond is a wide band gap semiconductor with $E_g = 5.45$ eV, but it can be easily doped with boron using an *in situ* Chemical Vapour Deposition (CVD) process. Due to the presence of boron, diamond effectively changes its electrical conductivity [12,13] and becomes a p-type semiconductor material. Such a material has remarkable electrochemical features, i.e. chemical stability [14], a wide electrochemical window [15] and high anodic stability [16].

Boron-doped diamond films are commonly used as an electrode material in the applications related to hazardous organic compounds or sensing [12,16,17]. Moreover, due to the biocompatibility of BDD, it is a great material for sensing various kinds of proteins or DNA [18,19]. In this case, nanocrystalline boron-doped diamond films appear to be a promising material for optically transparent electrodes (OTEs) [2]. In the available literature, a few reports can be found that focus on optically transparent boron-doped diamond electrodes. Stotter et al. [2,20] employed boron-doped diamonds electrodes in spectroelectrochemistry studies in the UV wavelength region which showed good

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transparency at 50–60%. Mermoux et al. [21] used confocal Raman imaging to study OTEs in samples with a thickness of 380 μm. Moreover, Gao et al. [22] used BDD in a biochemical application for detecting current spikes caused by the oxidation of catecholamine molecules released from mouse adrenal chromaffin cells.

Several authors reported on the optical properties of B-NCD films but only in a limited wavelength range. Hu et al. [23] and Gupta et al. [24] showed ellipsometric angles Ψ, Δ and dielectric constants in a range of 200–1230 nm (1.0–5.5 eV). Zimmer et al. [7] investigated heavily boron-doped nanocrystalline diamond films using spectroscopic ellipsometry; the obtained results included Ψ, Δ, total reflectance and optical constants in the VIS–NIR range (up to 950 nm). When there is a need to design a sensor combining different materials or optically transparent coating, information about optical constant and transmittance becomes crucial. In the published literature, the pertinent data for a broader wavelength range is still lacking (e.g. windows for telecommunication or FT-IR applications). Furthermore, in order to achieve silicon–diamond optical structures ($n_{Si} = 3.48$, $n_{diamond} = 2.42$ at 1550 nm), the highest possible refractive index of B-NCD films is needed.

In addition, boron doping has a crucial impact not only on electronic properties but also on optical properties of diamond. Boron dopant introduces an acceptor level located at 0.38 eV from the top of the valence band [13,25].

To the best of our knowledge, a description of opto-electrochemical properties of ultrathin B-NCD films in the broad wavelength range have yet not been published. In this paper, we report on the deposition of sub 100 nm ultrathin B-NCD films on silicon substrates at the low temperature of 500 °C, and on the outcome of the investigation of optical and electrical properties of these films.

The use of truncated cone-shaped substrate holder enables a local increase in the electric field by changing the reactor geometry. This phenomenon allows achieving high microwave power densities at moderates pressures [26,27]. Increase in the microwave power density results in the high sp^3 content, small roughness, lower growth rate, and effective boron incorporation [28].

The optical properties such as, optical constants, dielectric constant and transparency over a broad wavelength (from 200 nm to 20 μm) were investigated. Diamond processes were performed by microwave plasma assisted chemical vapour deposition (MW PA CVD). The numerical analysis of scanning electron microscopy (SEM) and atomic force microscopy (AFM) was applied to investigate the morphology of nanocrystalline diamond films. The chemical composition of the films was investigated by means of micro-Raman spectroscopy. Cyclic voltammograms were recorded to determine the electrochemical window and reaction reversibility at the electrode. The thickness and optical properties in the UV–MIR wavelength range, i.e. refractive index and extinction coefficient were estimated using spectroscopic ellipsometry (SE). Also, the optical band gap energy E_g was obtained using Tauc's plot.

2. Experimental

2.1. CVD nanodiamond film deposition

B-NCD films were synthetized in an MW PA CVD system (SEKI Technotron AX5400S, Japan) on highly doped single-crystal p-type Si (100) and low-doped silicon wafers used as reference samples for electrical characterization. In our experiments, we used home-made nanodiamond suspensions, i.e. diamond particles with a mean size of 7–25 nm suspended in dimethyl sulfoxide (DMSO) by high power sonication process. The substrates were seeded by sonication in nanodiamond suspension for 30 min [29,30]. The substrate temperature was maintained at 500 °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) [31,32]. 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 at 300 sccm of the total flow rate. The base pressure was about 10^{-6} Torr and the process pressure was kept at 50 Torr. The boron level expressed as the [B]/[C] ratio in the gas phase was 0, 2000, 5000 or 10,000 ppm. Diborane (B_2H_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 h, producing nanocrystalline films of a thickness less than 100 nm.

2.2. Electrochemical and electrical 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_2SO_4 at a scan rate of 0.1 V 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 electrochemical impedance spectroscopy measurements were carried out in 0.5 M Na_2SO_4, with Pt mesh as a counter electrode and an Ag/AgCl/0.1 M KCl electrode as a reference electrode. The used frequency ranged from $f = 20$ kHz to 0.1 Hz with a 10 mV amplitude of the AC signal. The impedance spectra were recorded in the range from +0.8 to −0.8 V (with a 0.05 V step) vs. Ag/AgCl/0.1 M KCl. Before each impedance measurement, the potential was held for 1 min. The resistivity values at room temperature were measured by four-point probe placed in a straight line with equal interprobe spacing ($s = 1.5$ mm). The needle-like probes with a radius of 100 μm were utilized. The sample size was 1 × 1 cm. The correction factor of 0.86 was taken into account during resistivity estimation due to the finite sample size [33,34]. A source meter (Keithley 2400, UK) was used as a current source applied to the external probes. The current was gradually increased from 0 up to 100 μA with a step of 1 μA. Voltage on the internal probes was measured with a VA multimeter (Appa 207, Taiwan). Each sample was measured at four surface points and the mean resistivity was calculated.

The reference samples of B-NCD deposited on low-doped silicon wafers were used for electrical characterization. The reference samples and Si/BDD electrodes were deposited simultaneously during the same CVD process. Both sample types showed similar BDD film thickness, as measured by profilometer.

A special pre-treatment procedure of deposited B-NCD electrodes was performed to increase the electrochemical performance as reported elsewhere [35,36].

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 surface topography was examined with an atomic force microscope (AFM) (Innova, Bruker, USA). The imaging tapping mode and standard Si tips were used to perform the surface characterization. The scan size was 2 × 2 μm.

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