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# The structural and electrochemical properties of boron-doped nanocrystalline diamond thin-film electrodes grown from Ar-rich and $H_2$-rich source gases

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## ABSTRACT

The microstructural, electrical and electrochemical properties of boron-doped (ultra)-nanocrystalline diamond (UNCD) films deposited from a $CH_4/H_2/Ar$ source gas mixture were compared with those of boron-doped nanocrystalline diamond (NCD) films grown from a conventional $CH_4/H_2$ source gas mixture. Scanning electron microscopy, visible-Raman spectroscopy and X-ray diffraction analysis were employed to probe the film morphology and microstructure. Conducting-probe atomic force microscopy (CP-AFM) was used to simultaneously map the morphology and electrical conductivity of the two film types. Spatial heterogeneity in the electrical conductivity was observed for both films as each is composed of regions of high electrical conductivity isolated by more insulating regions. The electrochemical properties were evaluated using the redox couples: $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2-/3-}$, methyl viologen, dopamine, and $Fe^{3+/2+}$. Taken together, the results confirm that even though the morphology and microstructure of UNCD and NCD films are distinct, both boron-doped film types exhibit comparable electrical and electrochemical properties.

## 1. Introduction

It has been reported that diamond films from different sources exhibit reproducible electrochemical behavior [1,2]. This is an important observation as conductive diamond is a new type of carbon electrode material so it is critical that the materials commercially available to researchers exhibit the properties expected for high quality diamond and that the properties are reproducible from source to source. Furthermore, it has been shown that boron-doped microcrystalline ($H_2$-rich growth) and (ultra)-nanocrystalline (Ar-rich growth) diamond film electrodes possess similar electrochemical properties [2,3]. In general, there are several factors that influence the electrochemical response of a polycrystalline diamond film: (i) the presence of non-diamond $sp^2$-bonded carbon, (ii) the surface termination (H vs. O), (iii) the dopant type, level, and distribution and (iv) grain boundaries and other morphological defects. The extent to which any one of these factors influences the electrode response will depend on the charge-transfer mechanism for the redox analyte being tested [1–8]. The electric double layer structure formed at diamond, which is likely different from the structure at other carbon electrodes, will also affect the electrochemical response. This occurs through effects on the electric field strength felt by the analyte at the plane of closest approach where the electron transfer occurs.

To date, there are two procedures for preparing nanocrystalline boron-doped diamond thin films. One procedure, developed by the Naval Research Laboratory (NRL) group, involves use of a conventional $CH_4/H_2$ source gas mixture, so-called nanocrystalline diamond (NCD) [9–13]. Another method, developed by the Argonne National Laboratory group, involves the use of a $CH_4/H_2/Ar$ source gas mixture, so-called (ultra)nanocrystalline diamond (UNCD) [3,13–20]. CVD deposition of NCD from an $H_2$-rich gas mixture is similar to that for conventional microcrystalline diamond [9–13,21]. These films are faceted but the crystal size is small due to the short growth time and the high initial nucleation density that is achieved by proper substrate preparation and seeding. Films deposited from an Ar-rich mixture, on the other hand, are not faceted but rather possess a nodular morphology with negligible crystal faceting [3,13–20]. Theoretical results suggest that the nanocrystalline morphology results, at least in part, because of a high rate of renucleation due to $C_2$ dimer [14,16,22,23]. These UNCD films are very different from the NCD films as the former possess a smaller grain size, more grain boundaries, and $sp^2$-bonded carbon atoms in these grain boundaries. Our group and others have reported on the structural and electrochemical properties of nitrogen-incorporated and boron-doped nanocrystalline diamond from $CH_4/H_2/Ar$ source gas mixtures [2,3,15,17,24–26]. To better understand the relationship between the microstructure of boron-doped diamond thin film and its electrical and electrochemical properties, we employed conductive probe atomic force microscopy (CP-AFM) and scanning electrochemical microscopy (SECM) to study the spatial heterogeneity of these

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properties [27,28]. Both films are characterized by spatially heterogeneous electrical and electrochemical properties due, in part, to the inhomogeneous distribution of boron dopant atoms.

We report herein on an investigation of the morphological, microstructural, electrical, and electrochemical properties of boron-doped nanocrystalline diamond thin films deposited using Ar-rich (UNCD) and $H_2$-rich (NCD) source gas mixtures. We sought to determine the similarities and differences in the structural properties of these two film types and how these properties affect the material's electrochemical behavior. Atomic force and scanning electron microscopy (SEM), visible-Raman spectroscopy, and X-ray diffraction analysis were used to probe the film morphology and microstructure, respectively. Conducting-probe atomic force microscopy (CP-AFM) was used to simultaneously map the morphology and electrical conductivity of the two film types. $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$, $IrCl_6^{2-/3-}$, methyl viologen, dopamine and $Fe^{3+/2+}$ were redox systems used to assess the electrochemical behavior of the two film types.

## 2. Experimental

The UNCD films were deposited using microwave-assisted chemical vapor deposition (CVD) (1.5 kW, 2.54 GHz, Astex, Lowell, MA) on highly conducting p-Si (111) (0.05 cm thick × 1 $cm^2$ in area, ~$10^{-3}$ Ω cm, Virginia Semiconductor Inc., Fredricksburg, VA), as described in previous work [1–3,15,17]. The films were deposited using a 1% $CH_4$/5% $H_2$/94% Ar source gas mixture for 2 h. The flow rates were 1, 5 and 94 sccm, respectively. The low percentage of $H_2$ was necessary to obtain a stably positioned plasma. The microwave power and system pressure were maintained at 800 W and 140 Torr, respectively. The substrate temperature was ca. 800 °C. The physical properties of these films have been reported on elsewhere [2,3,15,17]. Boron doping was accomplished by added 10 ppm $B_2H_6$ (from a 0.1% $B_2H_6/H_2$ gas mixture) to the source gas. The resulting film thickness was ca. 4 μm. The carrier concentration was in the low $10^{20}$ $cm^{-3}$ range with a hole mobility between 0.1 and 1 $cm^2$/V s, as determined from Hall measurements. The film's electrical resistivity, as measured by a 4-point probe apparatus, was ≤0.01 Ω cm.

A high-quality, hydrogen-terminated boron-doped NCD film was deposited on a 3 in. diam. Si substrate. The sample was grown in an Astex PDS-18, 2.45 kHz microwave plasma reactor [9–12]. The unseeded silicon wafer was placed in the reactor and exposed to the microwave plasma for 8 min at a system pressure of 15 Torr, a substrate temperature of 750 °C, and a microwave power of 800 W. A gas composition consisting of 900 sccm $H_2$, 4 sccm of 0.1% $B_2H_6$ in $H_2$, and 7 sccm $CH_4$ flowed through the chamber. The wafer was then removed and seeded with ultra-disperse nanodiamond particles in an ethanol suspension in an ultrasonic bath, rinsed with ethanol, and dried with dry nitrogen. The seeded wafer was retuned to the chamber for growth (720 min) at a substrate temperature of 750 °C, a system pressure of 15 Torr, and a microwave power of 800 W. The gas composition flowing through the reactor was 900 sccm $H_2$, 4 sccm of 0.1% $B_2H_6$ in $H_2$, and 3 sccm $CH_4$. The resultant film was ca. 1.5 μm thick. The actual boron-doping level in this film was not measured, but the film had an in-plane resistivity near 0.01 Ω cm, similar to the UNCD films.

The electrochemical measurements were performed in a single compartment glass cell using a CHI 650 digital potentiostat (CH Instruments Inc., Austin, TX). A homemade Ag/AgCl (3 M KCl) electrode was used as the reference and a large-area carbon rod served as the counter electrode. The diamond film electrode was pressed against the bottom of the glass cell with the fluid being contained by a Viton O-ring [29]. The exposed geometric area was ~0.2 $cm^2$. The large-area counter electrode (carbon rod) was placed normal to the working electrode. The reference electrode was positioned near the working electrode using a cracked glass capillary. Electrical connection was made to the diamond by scratching the backside of the Si substrate with a diamond scribe and then coating the area with graphite from a pencil before contacting the Cu current collecting plate. The Cu plate was polished clean prior to contact. All measurements were made at room temperature (23 ± 2 °C) in solutions deoxygenated by a nitrogen purge gas. The diamond film working electrode was rinsed with ultrapure water, soaked for 20 min in distilled 2-propanol, and rinsed with ultrapure water again prior to use. A three-step cleaning procedure was used for all glassware: washing in a KOH/methanol bath, washing in a liquid detergent/water bath (Alconox, Inc.), and rinsing with ultrapure water.

CP-AFM measurements were performed in air using a modified NanoScope IIIa scanning probe microscope (Digital Instruments, CA). A gold-coated, pyramidally shaped silicon nitride tip mounted on a rectangular cantilever (Veeco NPG-20, radius of curvature less than 50 nm, tip height 15–20 μm, and full tip cone angle less than 35°) was used in the contact mode. The boron-doped diamond film was attached to a metal pod and electrical contact was made between the pod and the conducting Si substrate with Ag paint. A bias voltage of ±0.2 V was applied to the sample relative to the tip. Conductivity maps were recorded simultaneously with the topographic images. The conductivity measurement was made using a home-made current-to-voltage converter circuit [28]. This circuit converts the current flowing through the probe tip to a proportional output voltage that is then sent to a computer through the Signal Access Module (Digital Instruments, CA) of the microscope. The measurable current range was between ±6.5 μA.

Raman spectra were acquired at room temperature using a RAMAN 2000 spectrograph (Chromex, Inc., Albuquerque, NM) that consisted of a diode-pumped, frequency-doubled continuous wave (CW) Nd:YAG laser (500 mW at 532 nm, COHERENT), a Chromex 500 spectrometer (f/4, 600 grooves/mm holographic grating), and a thermoelectrically-cooled, 1024 × 256 element charge-coupled device (CCD) detector (ANDOR Tech., Ltd., South Windsor, CT). Spectra were collected with an incident power density of ca. 500 kW/$cm^2$ (100 mW at the sample and 5 μm diam. spot size) and a 10 s integration time. A white-light spectrum was collected under the same conditions and served as the background for spectral correction. The spectrometer was calibrated (wavelength position) with 4-acetamidophenol ($CH_3CONHC_6H_4OH$) and a high pressure, high temperature (HPHT), single crystal diamond sample (first-order phonon position = 1332 $cm^{-1}$).

SEM imaging was performed using a JSM-6300F (field emission) scanning electron microscope (JEOL Ltd., Tokyo, Japan, Center for Advanced Microscopy at MSU). The images were constructed from both secondary and backscattered electrons with an accelerating voltage of 10 kV. The film crystallinity was characterized by powder X-ray diffraction (XRD) using Cu Kα radiation with a wavelength of 1.5405 Å.

All chemicals were reagent grade quality or better and used without additional purification. Solutions (0.1 mmol/L) of potassium ferrocyanide (Aldrich), hexamineruthenium (III) chloride (Aldrich), potassium hexachloroiridate (IV) (Aldrich), methyl viologen dichloride hydrate (Aldrich), ferric sulfate (Matheson Coleman and Bell), and dopamine (Aldrich) were prepared. The supporting electrolyte for all solutions was either 1 mol/L KCl (Fisher Scientific) or 0.1 mol/L $HC1O_4$ (99.999%, Aldrich). All solutions were prepared with ultrapure water from a Barnstead E-Pure purification system (18 MΩ cm).

## 3. Results

### 3.1. Atomic force and scanning electron microscopy

Fig. 1 shows representative atomic force microscope (AFM) images (contact mode in air) of the UNCD and NCD films. Clearly, the morphology of the UNCD film is quite different from that of the NCD film. For example, the UNCD film has a cauliflower-like structure composed of clusters of small particles 30–50 nm in diameter. TEM images (not shown here) revealed that the small clusters are actually aggregates of diamond grains (grain size is ~15–20 nm) [2,3,14,17]. On the other hand, a more uniform morphology is seen for the NCD film that consists of small, faceted crystals. The crystal size ranges from