Supporting Information

Electroanalytical Performance of Nitrogen-Containing Tetrahedral Amorphous Carbon Thin-Film Electrodes

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Experimental

Electrode Preparation. Ta-C and ta-C:N films were grown on boron-doped Si (111 and 100) substrates ($\sim 10^{-3}$ Ω -cm) using pulsed laser-arc deposition (Laser-Arco system). This system works by laser-controlled, high pulsed-current cathodic vacuum arc deposition. In this process, a pulsed laser beam is rastered across a rotating graphite target (cathode) that is positioned near the substrate. Each laser pulse generates a small carbon-containing plasma discharge that rapidly expands away from the target toward the substrate (anode). Once the plasma reaches the substrate, a vacuum arc discharge is ignited between the target (graphite) and the substrate with peak currents approaching 1500 A. This deposition produces thin, but hard (30-60 GPa) and dense Ta:C films. The nitrogen-incorporated films were deposited in the presence of N₂ at flow

rates of 10, 30 or 50 sccm (ta-C:N). The substrate temperature during deposition was ca. 100 °C. The ta-C growth rate was approximately 2-3 $\mu\text{m/h}$. All films were grown on highly boron-doped Si (111 or 100) substrates at a nominal thickness of ca. 200 nm, as determined by a Dektak Profilometer.

Comparison measurements were made with glassy carbon (GC-20, Tokai Ltd.), that was polished to a mirror-like finish with decreasing alumina grit sizes (1.0, 0.3 and 0.05 μm diam.). The grit was slurried in ultrapure water and the polishing was done on individual felt polishing pads (Buehler Ltd.). After each polishing step, the electrode received an ultrasonic cleaning in ultrapure water for 20 min to remove polishing debris. As a final cleaning step, the electrode was ultrasonicated a second time for 20 min in ultrapure isopropanol. Like the ta-C films, the glassy carbon surface was cleaned by exposure to ultrapure isopropanol for 20 min prior to making an electrochemical measurement.

Comparison measurements were also made with polycrystalline diamond. The hydrogen-terminated boron-doped microcrystalline diamond thin films were deposited on highly boron-doped Si substrates using a procedure described previously.²⁹ Prior to the electrochemical measurements, the films were cleaned by immersion in ultrapure isopropanol for 20 min.

Film Characterization. Atomic force microscopy (AFM) was performed with a

NanoScope IIIa scanning probe microscope (Veeco Instruments Inc., CA) operating in the contact mode. Pyramidal-shaped Si_3N_4 tips, mounted on gold cantilevers (100 μm legs, 0.38 N/m spring constant), were used in air for obtaining the topographical images. Raman microprobe spectra were collected at room temperature using a Spex 1250 spectrograph with a 600 groove/mm holographic grating (Jobin Yvon-Horiba) and 514.5 nm light from an argon ion laser for excitation. The detector was a Symphony 2000 $\times$ 800 CCD (Horiba Jobin-Yvon) with a pixel size of 15 μm . X-ray photoelectron spectra (XPS) were recorded using a Perkin-Elmer Phi 5400 ESCA system (Perkin-Elmer) with a magnesium $\text{K}\alpha$ X-ray source (1254 eV). Samples were analyzed at a base pressure near 10^{-9} torr with a pass energy of 29.35 eV and a take-off angle of 45° . The spot size was roughly 250 μm^2 . The spectrometer was calibrated using the C1s line of graphite at 284.6 eV.

Electron Microscopy. HRTEM images were collected using a field-emission microscope (JEOL-2200FS, Tokyo, Japan) operating at 200 keV. Electron energy loss spectra (EELS) were recorded with a Gatan 1024x1024 detector for high quality STEM imaging and simultaneous EELS data collection. For the TEM images, a small thin section of a Ta:C or a diamond film was placed on a Formvar/carbon-coated copper grid (Ted Pella #01883-F). EELS line scans were collected in STEM mode with an e-beam spot size of 0.7 nm. To limit any EELS background signal from the carbon-coated grid, signal was only collected only from film sections in the voids of the grid.

Electrochemical Measurements. The electrochemical measurements were carried out in a single compartment glass cell using a CHI 650B potentiostat (CH Instruments, Inc., Austin, TX). A commercial Ag/AgCl “no-leak” electrode (3 M KCl, Dionex Corp.) was used as the reference and a platinum gauze served as the counter electrode. All of the films were pressed against a Viton o-ring placed at the bottom of the cell. The exposed geometric area was 0.2 cm². All solutions were deoxygenated by purging with N₂ for 15 min prior to and blanketed with the gas during a measurement. All measurements were made at room temperature (23 ± 2°C)

Chemicals. All solutions were prepared with ultrapure water from a Barnstead E-Pure system (>17 MΩ-cm). The potassium ferrocyanide (Sigma-Aldrich), hexamineruthenium (III) chloride (Aldrich), potassium hydroxide (Sigma-Aldrich), methylene blue (Sigma-Aldrich), potassium chloride (Sigma-Aldrich), potassium phosphate monobasic (Spectrum Chemical MFG), potassium phosphate dibasic (Columbus Chemical Industries), sulfuric acid (Columbus Chemical Industries) and hydrochloric acid (Columbus Chemical Industries) were reagent-grade quality and used without additional purification. All glassware was cleaned using a three-step procedure: ethanol/KOH bath, alconox/ultrapure water solution, and ultrapure water rinse.

Results

XPS analysis. Figure S-1A shows survey scans for a ta-C film deposited without N₂ and one deposited with 30 sccm N₂ added to the process gas. Clearly, nitrogen is present (N1s ~402 eV) in the near surface of only the film deposited in the presence of N₂. Both

film surfaces contain carbon (C1s ~284 eV) and oxygen (O1s ~532 eV). Figure S-1B shows both scans on an expanded scale, specifically enlargement of the C1s and N1s regions. The C1s line position is about 284.8 eV for both films; a slightly higher binding energy than that for carbon in graphite at 284.6 eV. This is consistent with there being some sp^3 carbon in the film.³⁰ Figure S-1C shows plots of the O/C and N/C atomic ratios for the different ta-C films deposited with varying amounts of N_2 .

AFM Analysis. Figure S-2 presents height-mode AFM images ($3 \times 3 \mu m^2$) for the ta-C and ta-C:N films. Based on the image features, all the films are characterized by a nodular morphology. The nodular features increase in size with increasing nitrogen content.

Raman analysis. The sp^3 carbon fraction and the configuration of the sp^2 domains in diamond-like carbon films can be deduced from the position of the D ($\sim 1360 \text{ cm}^{-1}$) and G ($\sim 1550 \text{ cm}^{-1}$) bands, the ratio of the peak areas and the peak widths. ta-C materials typically exhibit a predominant G-band. Figure S-3 shows the visible (514.5 nm) Raman spectra for ta-C and ta-C:N films between 800 and 2000 cm^{-1} . The spectra are characterized by an asymmetric scattering profile between 1000 and 1700 cm^{-1} , with a maximum at *ca.* 1510 cm^{-1} . Such spectra are typical for ta-C films.³³ The peak becomes more asymmetric with increasing nitrogen incorporation as the scattering intensity near 1350 cm^{-1} increases. This trend is indicative of an increasing fraction of sp^2 -bonded carbon. The Raman spectrum for amorphous carbons, like ta-C, is

dominated by modes of the graphitic lattice; the so-called D and G modes.³⁴ This domination is because of the sizably larger (230x) scattering cross-section coefficient for the sp^2 -bonded carbon.³⁵⁻³⁶ The G mode for amorphous carbons arises from the bond stretching vibrations of pairs of sp^2 sites, and the D mode is due to the breathing mode of six-fold sp^2 rings.³⁷

To estimate the sp^2/sp^3 carbon ratio in the films, the spectra were fit with two Gaussian-Lorentzian peaks: the D-mode centered at 1358 cm^{-1} and the G-mode at 1580 cm^{-1} .³³ An example of the peak fitting is presented in Figure S-3 for the 50 sccm ta-C:N film.

Figure S-1. (A) XPS survey spectra for a ta-C film and a ta-C:N film deposited with 30 sccm N₂. (B) Expanded XPS survey spectra for C1s and N1s peak from (A). (C) Plot of the O/C and N/C atomic ratio for different ta-C films as a function of the N₂ flow used during the deposition.

Figure S-2. Height-mode AFM images of ta-C and ta-C:N films deposited with 10, 30 and 50 sccm of N₂.

Figure S-3. Visible Raman spectra (514.5 nm) for ta-C and ta-C:N films deposited with 10, 30 and 50 sccm N₂.