

Optical and Electrochemical Properties of Optically Transparent, Boron-Doped Diamond Thin Films Deposited on Quartz

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The optical and electrochemical properties of transparent, boron-doped diamond thin film, deposited on quartz, are discussed. The films were deposited by microwave-assisted chemical vapor deposition, for 1–2 h, using a 0.5% CH₄/H₂ source gas mixture at 45 Torr and 600 W of power. A high rate of diamond nucleation was achieved by mechanically scratching the quartz. This pretreatment leads to the formation of a continuous film, in a short period of time, which consists of nanometer-sized grains of diamond. The thin-film electrode was characterized by cyclic voltammetry, atomic force microscopy, and UV–visible absorption spectrophotometry. The film's electrochemical response was evaluated using Ru(NH₃)₆^{3+/2+} in 1 M KCl, Fe(CN)₆^{3-/4-} in 1 M KCl, and chlorpromazine (CPZ) in 10 mM HClO₄. The film exhibited a low voltammetric background current and a stable and active voltammetric response for all three redox systems. The optical transparency of the polycrystalline film in the visible region was near 50% and fairly constant between 300 and 800 nm. The optical and electrical properties were extremely stable during 48-h exposure tests in various aqueous (HNO₃, NaOH) solutions and nonaqueous (e.g., chlorinated) solvents. The properties were also extremely stable during anodic and cathodic potential cycling in harsh aqueous environments. This stability is in stark contrast to what was observed for an indium-doped tin oxide thin film coated on quartz. The spectroelectrochemical response (transmission mode) for CPZ was studied in detail, using a thin-layer spectroelectrochemical cell. Thin-layer voltammetry, potential step/absorption measurements, and detection analytical figures of merit are presented. The results demonstrate that durable, stable, and optically transparent diamond thin films, with low electrical resistivity (~0.026 Ω·cm) laterally through the film, can be deposited on quartz.

The use of electrically conducting diamond as an optically transparent electrode (OTE) for spectroelectrochemical measurements has only recently begun to be studied.^{1,2} Diamond has a wide optical window, although not continuous, ranging from the

near-UV to the far-IR. Depending on the defect density, chemical composition, doping level, thickness, and grain size, boron-doped diamond films are transparent in the visible (300–900 nm) and far-infrared (<1100 cm⁻¹) regions of the electromagnetic spectrum.^{1,3} Moreover, the optical properties of diamond films can be manipulated and optimized through adjustments in the deposition conditions. The wide optical window, coupled with the interesting electrochemical properties, make diamond a new and unique material as an optically transparent electrode.^{1,2}

The present goal of our research is to determine the growth conditions that produce highly conducting (<0.05 Ω·cm) and optically transparent (>40%) boron-doped diamond thin films. Two approaches for the preparation of diamond OTEs are being evaluated: (1) free-standing diamond films¹ and (2) thin films deposited on optically transparent substrates, such as quartz.

The advantage of the diamond OTEs reported on herein, as compared to a traditional OTE, such as indium-doped tin oxide (ITO) on quartz, is its reproducible responsiveness and stability in harsh chemical environments. While ITO provides high conductivity and high optical throughput, we have found it to be unstable in strongly acidic and alkaline media and in chlorinated organic solvents, such as dichloromethane. A decrease in the electrical conductivity and an increase in optical transparency of ITO/quartz were observed after soak tests in these media, consistent with a loss of the ITO layer from the quartz surface.

We report on the optical, electrochemical, and spectroelectrochemical characterization of optically transparent, boron-doped diamond thin film, deposited on quartz. The results demonstrate that highly conducting, durable, and optically transparent diamond films can be reproducibly deposited on this substrate. The films possess a transmittance of 40–50% between 300 and 800 nm. Good electrode responsiveness is shown for chlorpromazine (CPZ), Ru(NH₃)₆^{3+/2+}, and Fe(CN)₆^{3-/4-} without any electrode pretreatment.

The electrical and optical properties are highly stable during exposure to strongly acidic and alkaline solutions, as well as to common organic solvents. The properties are also stable during anodic and cathodic polarization in strongly acid media. This stability is in stark contrast to what is observed for ITO during the same solution exposures and polarizations. Transmission spectroelectrochemical measurements were conducted in a home-made thin-layer cell to demonstrate the film's usefulness as an

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OTE. Thin-layer voltammetry, potential-step/absorption measurements, and detection analytical figures of merit are presented for CPZ in 10 mM HClO₄. The results presented portend the possibility of also growing these electrically conductive and transparent films on quartz waveguides and optical fibers for use in electrooptical sensors and detectors.^{4–8}

EXPERIMENTAL SECTION

Film Deposition. The quartz substrate (1 × 1 × 0.1 cm³) was prepared by mechanically scratching one side of the substrate with 0.1-μm diamond powder slurried in ultrapure water. After scratching, the diamond powder was removed through consecutive 5-min ultrasonications in ultrapure water, 2-propanol, acetone, 2-propanol, and ultrapure water. The substrate was then dried under a stream of nitrogen. A boron-doped film was deposited on the scratched quartz with a CH₄/H₂ volumetric ratio of 0.5%, 10 ppm B₂H₆ dopant, a total gas flow of 100 sccm, a gas pressure of 45 Torr, and microwave power of 600 W. The substrate temperature during deposition was estimated to be 800 °C, using an optical pyrometer. The growth time was either 1 or 2 h, followed by a 10-min hydrogen plasma treatment at 600 W and 45 Torr. This postgrowth treatment was applied to remove any adventitious sp²-bonded non-diamond carbon impurities and to hydrogen terminate the surface. The films were then cooled over a 2-min period by gradually reducing the power and pressure of the hydrogen plasma to 400 W and 10 Torr. The resulting films were 1 cm² and estimated to be ~500 nm in thickness after 1-h growth and ~1000 nm after 2-h growth.

Optical Measurements. The diamond and ITO OTEs were rinsed with distilled 2-propanol (IPA) and allowed to dry in air, prior to making any optical measurements. The electrodes were mounted vertically for UV–visible measurements and were placed orthogonal to and facing the incident light. The electrodes were held in place over the aperture of the sample holder, using a small piece of double-sided adhesive tape along one edge. The spectrum for an uncoated and unscratched quartz substrate, cleaned in the same manner, was used as the background. UV–visible spectra were recorded with a computer-controlled Shimadzu UV-2401 PC spectrophotometer (Shimadzu Corp., Columbia, MD), using a slit width of 5 nm and a 210 nm/min scan rate.

Electrochemical Measurements in the Standard Glass Electrochemical Cell. Electrochemical measurements were made with a computer-controlled potentiostat (model 650A, CH Instruments, Inc., Austin, TX) in a three-electrode configuration. No *iR* correction was used in any of the reported measurements. The electrodes were clamped over the bottom opening of a three-necked, glass electrochemical cell.⁹ A Viton O-ring (i.d. 0.5 cm), placed between the cell opening and the electrode surface,

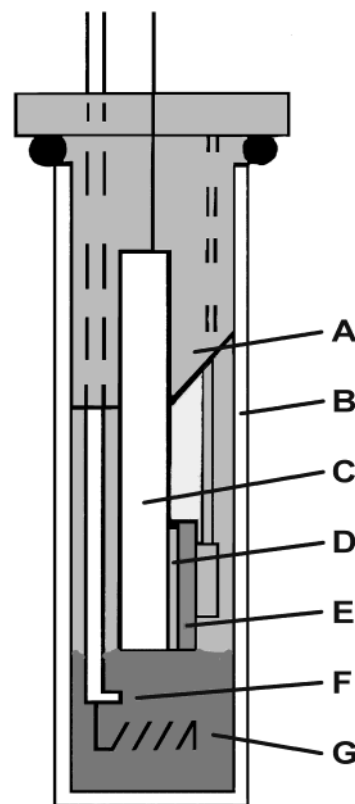


Figure 1. Diagram of the transmission thin-layer spectroelectrochemical cell: (A) Kel-F insert, (B) quartz cuvette, (C) polished quartz, (D) 150-μm silicone gasket, (E) boron-doped diamond OTE, (F) Ag-QRE, and (G) Pt auxiliary electrode.

ensured that a controlled nominal surface area of 0.2 cm² was exposed to electrolyte solution. Contact was made to the working electrode by pressing a piece of nickel foil on the surface. The foil was roughly the size of the electrode with a portion in the center removed just larger in diameter than the O-ring. A spacer was cut from a rubber sheet to the same dimensions of the nickel foil and was used to press the foil against the electrode surface. The O-ring was sonicated for 10 min in ultrapure water, rinsed with distilled IPA, and dried under a stream of nitrogen gas (before mounting a diamond electrode in the cell). Once mounted in the cell, the electrode was exposed to IPA and allowed to soak for 30 min. The electrode was then rinsed thoroughly with distilled water, and the cell was filled with the electrolyte solution of interest. Nitrogen was bubbled through the solution for 10 min, to remove dissolved oxygen. All measurements were made with the solution blanketed by a stream of nitrogen. The auxiliary electrode was a large-area carbon rod, and the reference was a commercial Ag/AgCl electrode filled with 4 M KCl saturated with AgCl. Both the auxiliary and reference electrodes were placed in fritted capillaries filled with the supporting electrolyte. The frit for the auxiliary electrode did not add significant resistance to the flow of current through the cell, as cyclic voltammograms for Ru(NH₃)₆^{3+/2+}, measured with and without the frit, were identically shaped.

Spectroelectrochemical Measurements in the Thin-Layer Cell. Cyclic voltammetric and potential-step/absorption measurements were carried out in a homemade, thin-layer cell. The design of the cell is shown in Figure 1. The main body of the cell is constructed with Kel-F plastic and optical-quality quartz. The entire

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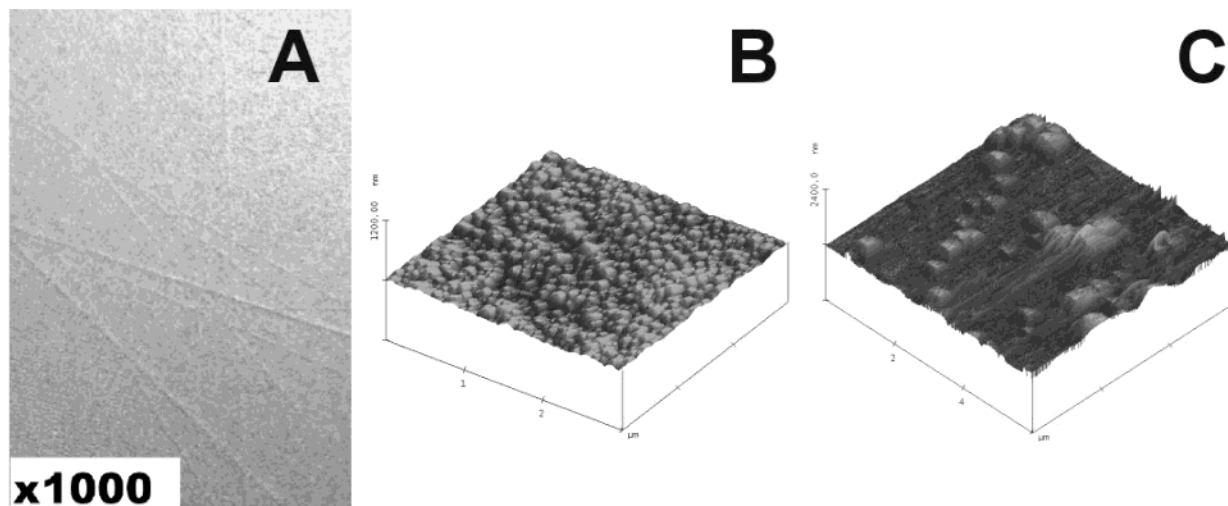


Figure 2. An (A) optical micrograph and (B) AFM image (height mode) of an as-grown, boron-doped diamond thin film deposited on a scratched quartz substrate for 1 h. (C) An AFM image (height mode) of boron-doped diamond deposited for 1 h on a poorly prepared quartz substrate.

body fits in a standard 10×10 mm quartz cuvette. A silicone rubber gasket, placed between the quartz insert and electrode surface, creates a thin-layer cavity $\sim 150 \mu\text{m}$ thick with a volume of $4.8 \mu\text{L}$. Electrical contact is made by pressing a complete edge of the electrode surface, unexposed to electrolyte solution, onto a Pt wire, which extends to the outside of the cell. Another coil of Pt wire is used as the auxiliary electrode, and Ag wire is used as a quasi-reference electrode (QRE). The thin-layer cavity is open at the bottom, allowing it to be filled with electrolyte solution through capillary action when the quartz cuvette is partially filled with solution. The auxiliary and reference electrodes are positioned in the electrolyte solution (below the cell insert) in the assembled and filled cell.

Soaking Experiments with Indium-Doped Tin Oxide Films. ITO films with a nominal thickness of 20 nm and a resistivity of $3.7 \times 10^{-5} \Omega \cdot \text{cm}$, deposited on fused quartz microscope slides (Delta Technologies, Limited, Stillwater, MN), were cut into $\sim 1 \text{ cm}^2$ pieces by scoring along the uncoated surface and breaking. The pieces were sequentially soaked for ~ 48 h in neat toluene (MCB Manufacturing Chemists, Inc., ACS), hexane (Baker, ACS, 97%), methanol (Baker, ACS, 99.8%), dichloromethane (Mallinckrodt, ACS), 1 M HNO_3 (Cleveland Chemical Industries, 70% ACS), or 1 M NaOH (Spectrum, ACS). The aqueous solutions were prepared with ultrapure water. The UV–visible transmittance spectrum (as described above) and in-plane resistivity were recorded before and after soaking.

Four-Point Probe Measurements. The resistivity of the diamond and ITO films was measured with a tungsten-tip, four-point probe connected to an HP 3478A multimeter (Hewlett-Packard, Palo Alto, CA), which was operated in the four-wire resistance measurement mode. The probe spacing was 0.1 cm. The measured resistance was converted to resistivity according to the equation,¹⁰

$$R_s(\Omega \cdot \text{cm}) = 4.532tR(\Omega)$$

where t is the film thickness in centimeters. Six measurements were made at different locations on each film. The nominal resistivity of the diamond OTE was $0.026 \Omega \cdot \text{cm}$.

Atomic Force Microscopy (AFM). Atomic force micrographs were captured in the contact mode (in air) with a Nanoscope IIIa instrument (Digital Instruments/Veeco Metrology Group, Santa Barbara, CA), using $200\text{-}\mu\text{m}$ narrow-leg, triangular cantilevers having a spring constant of 0.06 N/m .

Chemicals. KCl (1 M, Mallinckrodt ACS, or Baker ACS, 99.9%), 0.1 M NaOH (Mallinckrodt ACS, 99%), and 10 mM HClO_4 (Aldrich, 70% in water from 99.999%) were each prepared once a week with $18 \text{ M}\Omega$ ultrapure water from a Barnstead E-pure water purification system. $\text{K}_4\text{Fe}(\text{CN})_6$ (Aldrich ACS, 99%), $\text{Cl}_3\text{Ru}(\text{NH}_3)_6$ (Aldrich ACS, 98%) in 1 M KCl, and chlorpromazine hydrochloride (Sigma) in 10 mM HClO_4 were all prepared fresh daily.

RESULTS AND DISCUSSION

An ideal diamond OTE for UV–visible spectroelectrochemical measurements would be an ultrathin film with a nominal grain size less than the wavelength of light, to minimize light absorption and scattering losses, respectively. Pretreatment of the quartz by uniform scratching is necessary to achieve this type of film. The scratching produces a high nucleation-site density on an otherwise smooth quartz surface with the resulting grooves, if thoroughly cleaned of the polishing debris, serving as the nucleation sites. *This is a key step in the deposition process!* The high nucleation rate leads to growth of a thin and continuous submicrometer grain film. An optical micrograph of a film grown for 1 h on a scratched substrate is shown in Figure 2A (collected with a polarization filter). The film is continuous over the surface with no apparent pinholes or void spots. The adhesion is superb, even after handling the electrode, as this one was, for many experiments. Some of the larger scratches on the quartz are visible through the diamond film, indicative of the film's optical clarity. The height-mode AFM image, presented in Figure 2B, shows a nodular film morphology with features having a nominal diameter of $\sim 100\text{--}200 \text{ nm}$. In contrast, the height-mode AFM image, presented in Figure 2C, illustrates the nature of diamond growth on a poorly prepared quartz substrate. Isolated clusters of large diamond grains are

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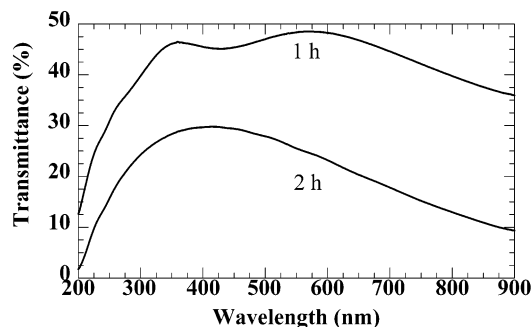


Figure 3. UV-visible transmission spectra for boron-doped diamond thin film deposited on quartz for 1 and 2 h. The films were deposited from a source gas mixture of 0.5% C/H and 10 ppm B₂H₆.

seen, and there is certainly no continuous film. This type of growth occurs if the surface is not uniformly scratched or the resulting grooves are not thoroughly cleaned of polishing debris. In this case, the rate of crystal growth exceeds the rate of nucleation, leading to isolated diamond deposition after 4 h.

Background-corrected UV-visible transmission spectra for two different diamond films, deposited on quartz, are shown in Figure 3. The morphology of both films resembles that shown in Figure 2B. For both the 1- and 2-h films, the transmittance significantly decreases below 300 nm, because of absorption by nitrogen impurities (i.e., electronic transitions from nitrogen impurity levels to the conduction band) and indirect band gap absorption below 225 nm (i.e., electronic transitions from the valence band to the conduction band). Nitrogen is a common impurity in chemical vapor deposition (CVD) diamond arising from either contamination of the source gases or atmospheric leaks into the reactor. The A aggregate of nitrogen, comprising a nearest-neighbor pair of substitutional nitrogen atoms, is the dominant impurity in most natural diamonds.¹¹ This A aggregate behaves as a deep donor with an ionization energy of 4 eV and may be responsible for the absorption between 225 and 300 nm. The transmittance of the 1-h film is relatively constant at 40–50% between 300 and 800 nm. The 2-h film is thicker and presents a longer path length, hence the reduced transparency. Preliminary measurements by our collaborators at NREL indicated that less than 10% of the throughput loss below 400 nm is due to reflectance. Reflectance losses gradually increase to 20% at wavelengths between 600 and 1000 nm. The 1-h film possessed low electrical resistivity ($\rho = 0.026 \Omega \cdot \text{cm}$) and high optical throughput; consequently, this OTE was used in the spectroelectrochemical measurements discussed below. It should be pointed out that films of this optical and electrical quality can be reproducibly prepared on quartz.

At least five factors can influence diamond's optical transparency in the near-UV and visible regions of the electromagnetic spectrum: (1) the substitutional boron in the lattice, which increases the optical density with a broad absorbance continuum above 600 nm, (2) scattering losses due to the polycrystalline morphology, (3) structural defects (e.g., grain boundaries) containing sp²-bonded carbon and boron, (4) chemical impurities, such as substitutional nitrogen, which result in absorption below 300 nm,^{11,12} and (5) reflectance losses. The transmission is affected across the spectral region investigated by changes in the effective

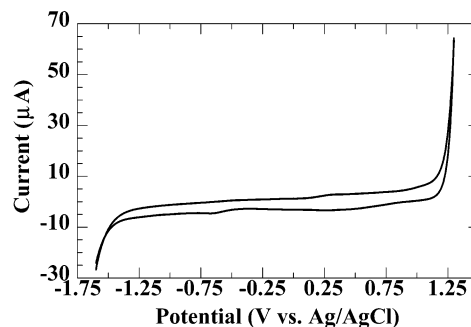


Figure 4. Cyclic voltammetric i - E curve in 1 M KCl for a diamond thin film deposited on quartz for 1 h. Scan rate, 25 mV/s. The film was deposited as described in Figure 3.

Table 1. Summary of Cyclic Voltammetric Data for a 1-h Diamond Thin Film Deposited on Quartz

redox system	ΔE_p (mV)	$E_{p/2}$ (mV vs Ag/AgCl)	i_p^{ox} (μA)	$i_p^{\text{ox}}/i_p^{\text{red}}$	$Q_p^{\text{ox}}/Q_p^{\text{red}}$
Ru(NH ₃) ₆ ^{3+/2+}	59	-165	5.0	0.99	1.1
Fe(CN) ₆ ^{3-/4-}	67	276	6.3	1.1	1.0
chlorpromazine	84	652	5.6	1.5	1.5

path length. The relatively unchanging transmission spectrum between 300 and 800 nm for the 1-h film is a useful feature for background correction. In our opinion, these optical data do not represent a limiting case. Rather, the optical throughput should be adjustable through controlled variations in the deposition conditions—a research task that is presently underway.

A background cyclic voltammetric i - E curve (in 1 M KCl) for the 1-h film is shown in Figure 4. This measurement and the voltammetric measurements discussed below, for which the data are summarized in Table 1, were made in a standard, single-compartment electrochemical cell. The response is featureless over the entire potential range, as expected, but the current magnitude is slightly larger than that normally observed for boron-doped diamond films deposited on Si substrates. The anodic current density at 0.1 V is 7 $\mu\text{A}/\text{cm}^2$, compared to $\sim 2 \mu\text{A}/\text{cm}^2$ for a diamond film on Si.^{9,13} The anodic current at 1.25 V is due to the onset of chlorine evolution, and the cathodic current at -1.6 V is attributed to hydrogen evolution. The shape of this curve, which was unchanging with repeated cycling, is typical for films void of appreciable quantities of electroactive, sp²-bonded carbon impurities on the surface.

Cyclic voltammetry was used to investigate the response of the 1-h film electrode for the following redox systems: 0.1 mM Ru(NH₃)₆^{3+/2+} + 1 M KCl, 0.1 mM Fe(CN)₆^{3-/4-} + 1 M KCl, and 0.1 mM CPZ + 10 mM HClO₄. A summary of the cyclic voltammetric data is presented in Table 1. The cyclic voltammetric ΔE_p for Ru(NH₃)₆^{3+/2+} is relatively insensitive to the surface microstructure and chemistry of diamond, and other electrodes such as glassy carbon, but is sensitive to the electronic properties (i.e., density of states) at the standard reduction potential for the couple.^{9,14,15} Therefore, this redox system is useful for probing

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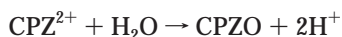
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the diamond film's electronic properties. ΔE_p is 59 mV at this scan rate (100 mV/s), indicating the electrode has a high density of electronic states at these potentials, sufficient to support rapid electrode-reaction kinetics. As expected for currents limited by semi-infinite linear diffusion, i_p^{ox} varies linearly ($r^2 > 0.99$) with the scan rate^{1/2}. The i_p^{ox}/i_p^{red} and Q_p^{ox}/Q_p^{red} ratios are near 1.0 for scan rates between 10 and 500 mV/s.

ΔE_p for $\text{Fe}(\text{CN})_6^{3-/4-}$ is relatively insensitive to the surface microstructure of diamond but is very sensitive to the electronic properties and surface chemistry.^{9,13} ΔE_p is very sensitive to the surface microstructure and chemistry of glassy carbon.^{14,15} Specifically, ΔE_p is much larger at diamond electrode surfaces terminated with oxygen functional groups than at surfaces terminated with hydrogen.¹³ The oxygen functional groups apparently block reaction sites that are available on the hydrogen-terminated surface; hence, the reaction kinetics are inhibited. Therefore, this redox system is useful for probing both the electronic properties and the extent of hydrogen termination. ΔE_p for this redox couple is 67 mV at this scan rate (100 mV/s), indicating the electrode has a high density of electronic states at these potentials and the surface is predominately hydrogen-terminated, even after the numerous electrochemical measurements that were performed. The i_p^{ox} for this analyte varies linearly ($r^2 > 0.99$) with the scan rate^{1/2}, indicating that the current is limited by semi-infinite linear diffusion of the reactant to the interfacial reaction zone. The i_p^{ox}/i_p^{red} and Q_p^{ox}/Q_p^{red} ratios are stable, near 1.0, for scan rates between 10 and 500 mV/s.

The cyclic voltammetric ΔE_p for CPZ is relatively insensitive to the surface chemistry and microstructure of diamond but is sensitive to the electronic properties.^{9,16} CPZ has also been shown to undergo rapid electron transfer at polished, glassy carbon (sp²-bonded carbon), behaving as an outer-sphere system with respect to electron transfer.¹⁷ CPZ shows a tendency to adsorb on glassy carbon, but inhibiting adsorption by surface modification has little effect on the electrode kinetics.¹⁷ No significant adsorption, however, has been found for hydrogen-terminated, boron-doped diamond (sp³-bonded carbon).^{9,16,18} ΔE_p for CPZ is relatively insensitive to surface chemistry at both surfaces.^{9,16,17} However, i_p^{ox} varies linearly with scan rate at glassy carbon, as expected for an adsorbed species, and it varies linearly with (scan rate)^{1/2} at diamond, as expected for a species diffusing to the interfacial reaction zone.¹⁶ CPZ undergoes two 1-electron oxidation reactions in acidic media.¹⁹



The first electron-transfer reaction to form CPZ^{+} is reversible, but the second reaction to form CPZ^{2+} is chemically irreversible,

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Table 2. Optical and Electrical Stability Tests of ITO/Quartz OTEs during 48-h Solution Exposures

solvent	$\Delta\% \text{ T at } 275 \text{ nm}$	ρ before soak ($\Omega \cdot \text{cm}$)	ρ after soak ($\Omega \cdot \text{cm}$)
toluene	−0.111	3.8×10^{-5}	3.8×10^{-5}
hexane	−0.113	3.8×10^{-5}	3.8×10^{-5}
methanol	−0.195	3.8×10^{-5}	3.7×10^{-5}
1 M NaOH	+30.7	3.8×10^{-5}	$> 10^3$
1 M HNO ₃	+40.2	3.7×10^{-5}	$> 10^3$
CH ₂ Cl ₂	+45.4	3.8×10^{-5}	$> 10^3$

because the dication product undergoes rapid reaction with water to form an electroinactive sulfone.^{19,20} The voltammetric results reported herein are for the first 1-electron redox reaction. The cyclic voltammetric i – E curve for 0.1 mM CPZ + 10 mM HClO₄ was very similar in shape to curves for diamond and glassy carbon published previously and had the characteristic shape of a redox reaction controlled by semi-infinite linear diffusion.^{9,16–19} The ΔE_p is 84 mV at 100 mV/s. The i_p^{ox} value varies linearly with the scan rate^{1/2} between 20 and 500 mV/s. These results indicate that the surface exposed to solution was predominately composed of sp³-bonded diamond with an insignificant amount of sp²-bonded amorphous carbon. The i_p^{ox}/i_p^{red} and Q_p^{ox}/Q_p^{red} ratios are greater than 1, and this is attributed to the fact that some production of CPZ^{2+} occurs during the forward sweep that undergoes hydrolysis and is, thus, unavailable for reduction during the reverse sweep.

Normally, with diamond films deposited on electrically conducting substrates, the current is passed through the diamond film and the conductive substrate to a metal current collector in contact with the backside of the substrate. In this case, however, such a current path was not possible, due to the electrically insulating quartz. Therefore, the current was passed laterally through the electrode to a metal current collector positioned at the edge of the film. The low ΔE_p values indicate that the grains are in good electronic communication with the grain boundaries, providing a low-resistance current pathway. Again, the resistivity of the diamond film is 0.026 $\Omega \cdot \text{cm}$. Preliminary Hall effect measurements by our collaborators at NREL revealed a carrier concentration of $\sim 4 \times 10^{20} \text{ cm}^{-3}$ and a resistivity of 0.059 $\Omega \cdot \text{cm}$.

The morphological, optical, and electrochemical stability of diamond and commercial ITO film OTEs were compared. In the first series of comparison measurements, ITO films, coated on quartz, were soaked for 48 h in different organic solvents, and strong acid and alkaline solutions with the optical properties and film resistivity recorded before and after. The results are summarized in Table 2. While no significant changes in either the optical or electrochemical properties were observed after exposure to methanol, hexane, or toluene, films soaked in 1 M HNO₃, 1 M NaOH, and dichloromethane showed significant increases in the optical transparency (presented as $\Delta\% \text{ T at } 275 \text{ nm}$) and electrical resistivity. The resistivity increased to at least $10^3 \Omega \cdot \text{cm}$, as this is the maximum value measurable in our system. Both changes result from partial to complete removal of the ITO from the quartz surface. HNO₃ (1 M), NaOH (1 M), and dichloromethane are apparently effective in dissolving the film from the substrate. In

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contrast, the optical transparency (40–50%) and resistivity (0.026 $\Omega\cdot\text{cm}$) of the diamond thin film were unchanged after soaking in any of the solutions.

In a second series of measurements, ITO films, coated on quartz, were anodically and cathodically polarized, using cyclic voltammetry, in 1 M HNO_3 and NaOH . Significant increases in the optical transparency and electrical resistivity were found after anodic and cathodic polarization in both electrolytes, more so in the acid. For example, the polarization, performed in HNO_3 (five scans) between 2.2 and -0.55 V with a maximum current density of $0.15\text{ mA}/\text{cm}^2$, caused the optical transparency at 275 nm to increase by 45% and the resistivity to increase to $10^3\text{ }\Omega\cdot\text{cm}$, or greater. Such a large increase in the transparency suggests that most of the ITO film was removed from the surface. In contrast, the morphological, optical, and electrical properties of the diamond film were unchanged after the polarizations in either HNO_3 or NaOH . For instance, the optical transparency (40–50%) and resistivity ($0.026\text{ }\Omega\cdot\text{cm}$) were unchanged after polarization in HNO_3 (10 scans) between 0.75 and -1.7 V with a maximum current density of $0.20\text{ mA}/\text{cm}^2$.

The reproducibility of the diamond OTE's optical and electrochemical properties was superb from film to film—better, in fact, than the ITO samples tested. On the other hand, ITO is notoriously variable, in terms of its chemical nature, the distribution of crystalline and amorphous regions, the tin and indium oxide and hydroxide content,²¹ and the electronic properties.²² The surface chemistry, modified by either intentional modification or adventitious adsorption of contaminants, can impact the properties of ITO, particularly the work function.²³ Thus, the heterogeneous nature of ITO often leads to significant variability in the optical and electrical properties from type to type.^{21–23}

The stability of the 1-h diamond OTE was further tested by measuring UV–visible transmission spectra, in the thin-layer spectroelectrochemical cell, during potentiodynamic cycling in 1 M KCl . Figure 5A shows spectra before polarization and after 15 and 30 cycles between -0.6 and $+1.2$ V versus Ag/QRE at a scan rate of $25\text{ mV}/\text{s}$. The anodic potential limit extends into the chlorine evolution region with a maximum current of $0.075\text{ mA}/\text{cm}^2$. Chlorine evolution, in general, is microstructurally damaging to sp^2 -bonded carbon electrodes.²⁴ Although this is a low-current density, there are no significant changes observed in the optical spectra and there also were no changes observed in the voltammetric response.

Figure 5B shows a series of transmission spectra, measured after removal from the thin-layer cell, for the same film before polarization, after 10 cycles over a 2.45-V potential range in 1 M HNO_3 , and after 5 cycles over a 2.25-V potential range in 1 M NaOH . The potential cycling in both media extended well into the hydrogen and oxygen evolution regions. Again, there is no significant variation in the transmission spectra after cycling in either solution.

Figure 6 presents a background-corrected cyclic voltammetric i – E curve for $0.1\text{ mM CPZ} + 10\text{ mM HClO}_4$, measured in the

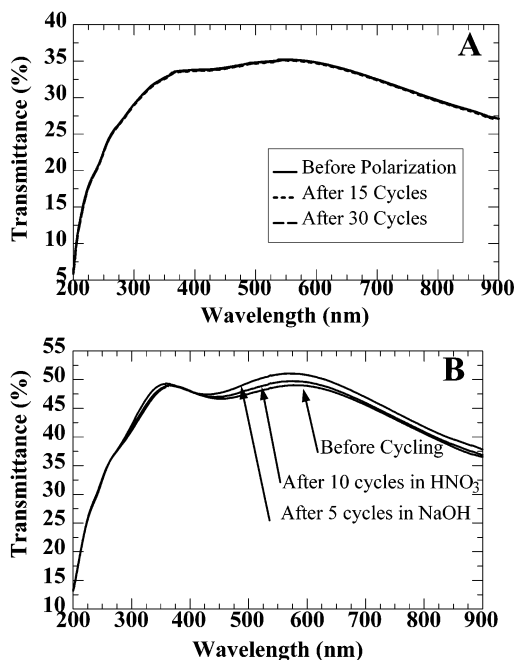


Figure 5. UV–visible transmission spectra for (A) a diamond thin film before and after 15 and 30 cycles in 1 M KCl and (B) the diamond film OTE before potential cycling and after 10 cycles in 1 M HNO_3 and 5 cycles in 1 M NaOH . The measurements were made in the thin-layer spectroelectrochemical cell, using 1 M KCl . The film was deposited as described in Figure 3.

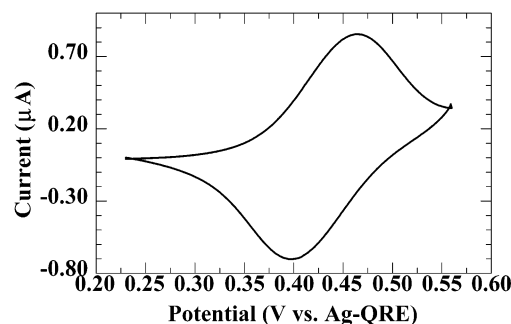


Figure 6. Background-corrected, thin-layer voltammetric i – E curve for a diamond thin film, deposited on quartz for 1 h, in 0.1 mM CPZ in $10\text{ mM H}_2\text{SO}_4$. Scan rate, $2\text{ mV}/\text{s}$. The film was deposited as described in Figure 3.

thin-layer spectroelectrochemical cell. The scan rate was $2\text{ mV}/\text{s}$. The $Q_p^{\text{ox}}/Q_p^{\text{red}}$ ratio is ~ 1 , and the peaks are approximately Gaussian in shape with no evidence of diffusion. i_p^{ox} and i_p^{red} varied linearly with the scan rate, while Q_p^{ox} and Q_p^{red} were independent of the scan rate. These observations are predicted for thin-layer voltammetric behavior.^{25–27} ΔE_p is 68 mV , larger than the 0 mV expected if the electrode kinetics are fast, relative to the scan rate. We believe the larger-than-expected ΔE_p is due, at least in part, to uncompensated resistance in the cell. The Q_p^{ox} value, $56\text{ }\mu\text{C}$, is consistent with the charge calculated for $4.8\text{ }\mu\text{L}$ of 0.1 mM CPZ ($n = 1$), $46\text{ }\mu\text{C}$. The peak current for a cyclic voltammetric i – E curve under thin-layer conditions is predicted to be^{25–27}

$$i_p = (9.39 \times 10^5) n^2 \nu V C_o^*$$

where n is the number of electrons transferred per equivalent, ν

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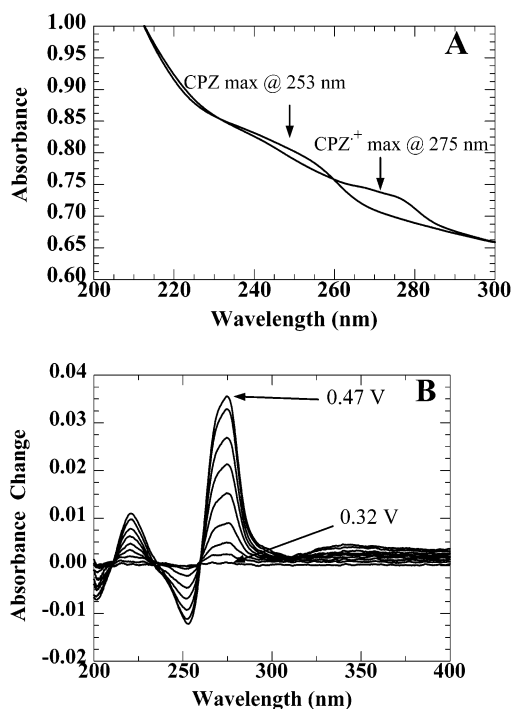


Figure 7. (A) UV-visible absorbance spectra at a diamond thin film, deposited on quartz for 1 h, for chlorpromazine (CPZ^0), at 0.30 V, and the oxidation product ($\text{CPZ}^{0/+}$), at 0.50 V, in the thin-layer cell. (B) A series of UV-visible absorbance spectra, using the same film, for 0.1 mM chlorpromazine in 10 mM HClO_4 , as the potential is stepped from 0.32 to 0.47 V vs Ag-QRE. The film was deposited as described in Figure 3.

is the scan rate (V/s), V is the cell volume (cm^3), and C_0^* is the bulk concentration (mol/cm^3). The i_p^{ox} value in Figure 6 of 0.86 μA , is in good agreement with the predicted value of 0.90 μA .

UV-visible spectroelectrochemical measurements for the first 1-electron-transfer reaction of chlorpromazine, $\text{CPZ}^{0/+}$, were performed, and the absolute spectra recorded during anodic (0.50 V) and cathodic (0.30 V) potential steps are presented in Figure 7A. The spectral changes for CPZ are recorded on a sloping background, as the diamond OTE exhibits a changing transmittance at these wavelengths (see Figure 3). CPZ has an absorbance maximum at 253 nm, due to a $\pi \rightarrow \pi^*$ transition ($\epsilon_0 \sim 10\,000 \text{ L}/\text{mol}\cdot\text{cm}$), while the radical cation produced by a 1-electron oxidation has an absorbance maximum at 275 nm.²⁰ This is presumably also due to a $\pi \rightarrow \pi^*$ transition ($\epsilon_0 \sim 20\,000 \text{ L}/\text{mol}\cdot\text{cm}$). In Figure 7B, a series of difference spectra (oxidized form – reduced form) are presented for different applied potentials. As the potential is stepped positively from 0.32 to 0.47 V, the peak at 253 nm gradually decreases and the peak at 275 nm increases. A peak at 224 nm also develops as the applied potential is made more positive. The spectral features can be reversibly formed with changes in the applied potential. A background spectrum for the cell containing fully reduced CPZ was subtracted from each of the spectra to present the absorbance changes relative to a flat baseline. When overlaid, the spectra show well-defined isosbestic

points. The isosbestic point near 260 nm indicates that the species responsible for the absorbance peaks on either side of the point are stoichiometrically related. Here, these peaks are due to CPZ and $\text{CPZ}^{0/+}$.

A calibration curve was constructed, based on the absorbance change at 275 nm as a function of solution concentration. The plot was linear between 20 μM and 1 mM with a linear regression correlation coefficient of 0.9996 and a near-zero (0.0095 AU) ordinate intercept. The absorbance change was measured during a potential step from 0.30 to 0.50 V. This linear response curve indicates that the diamond OTE provides an analytically useful signal for the detection of CPZ. A 0.5 μM limit of detection ($S/N = 3$) is estimated from the data. A Nernst plot of applied potential versus $\ln [O]/[R]$, calculated from absorbance changes at 253 nm, was also constructed. The plot was linear, as predicted, with a linear regression correlation coefficient of 0.9990, and has an intercept of 0.41 V, close to the $E_{p/2}$ of 0.43 V, determined from the thin-layer cyclic voltammetric i - E curve presented in Figure 6. The slope of this plot was 56.9 mV, and is close to the $59.2/n$ mV ($n = 1$) predicted by the Nernst equation. The slope also indicates that the oxidation of CPZ to $\text{CPZ}^{0/+}$ involves the loss of 1 electron.

SUMMARY

The electrochemical and optical properties of a boron-doped diamond OTE were evaluated. The diamond OTE is a thin (<1000 nm) film deposited on quartz and exhibits superior morphological, optical, and electrical stability during exposure to strongly acidic and alkaline solution and chlorinated organic solvents. The diamond OTE also exhibits superior stability during anodic and cathodic polarization in strongly acidic or alkaline media. Good electrochemical responsiveness is observed for $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{Fe}(\text{CN})_6^{3-/4-}$, and $\text{CPZ}^{0/+}$ without any electrode pretreatment. The diamond OTE has a high carrier concentration, $\sim 10^{20} \text{ cm}^{-3}$ (holes), and low electrical resistivity ($\sim 0.026 \Omega\cdot\text{cm}$) laterally through the grains and grain boundaries. The material has a high density of electronic states between -0.35 and 0.8 V versus Ag/AgCl, sufficient for rapid electrode reaction kinetics. The spectroelectrochemical performance of the diamond OTE was evaluated in a specially designed, thin-layer cell, using chlorpromazine. Well-defined, thin-layer voltammetry is observed with Q_p^{ox} values independent of scan rate, as expected for thin-layer behavior. For CPZ measurements, the linear dynamic range is from 20 to 100 μM and the estimated limit of detection is 0.5 μM ($S/N = 3$). A linear Nernst plot is observed with a slope of 56.9 mV, reflective of 1 electron being transferred per equivalent during the oxidation of CPZ to $\text{CPZ}^{0/+}$ and an ordinate intercept of 0.41 V.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation (CHE-9983676), the Center for Fundamental Materials Research at Michigan State University, and a NATO Scientific Collaboration Linkage Grant. Some optical and all Hall effect measurements were made by Dr. David Young at NREL. The assistance of Vada O'Donnell and Jennifer Wood with the preparation of the manuscript is much appreciated.

Received for review May 28, 2002. Accepted September 24, 2002.

AC0203544

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