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Differential pulse voltammetry of toxic metal ions at the boron-doped CVD diamond electrode

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Boron-doped polycrystalline diamond films were grown over a molybdenum substrate by a microwave plasma CVD process using a methane and hydrogen gas mixture at a pressure of 35 ± 1 Torr. Boron doping of diamond was achieved *in situ* by using a solid boron source while growing diamond in the CVD process. We have observed a negligible background current (ΔI) for diamond by differential pulse voltammetry in 0.5 M NaCl, 0.5 M H_2SO_4, and 0.5 M HNO_3 solutions over a wide potential range. Therefore, diamond will certainly have a use as an electrode material in electroanalytical applications to detect trace toxic/nontoxic metal ions such as cadmium, lead, copper, and silver. Differential pulse voltammetry was used to detect and evaluate the presence of lead ions in 0.5 M NaCl and cadmium ions in 0.5 M H_2SO_4 supporting electrolyte solution using highly conducting boron-doped diamond coated molybdenum electrode material. Furthermore, reverse differential pulse voltammetry was used to evaluate the presence of copper and silver ions in 0.5 M H_2SO_4 and 0.5 M HNO_3 solution, respectively. Diamond electrode has been used in this study to detect metallic ions in the solution over a wide potential range that covers +0.8 V to −0.4 V vs., SHE. © *1999 Kluwer Academic Publishers*

1. Introduction

Diamond is a unique material for innumerable applications because of its unusual combination of physical and chemical properties [1]. Therefore, several potential applications can be anticipated in electronics, optics, protective corrosion resistant coatings, bioelectroanalytical and detection of toxic trace metal ions in hazardous/hostile chemical environments.

Determination of toxic metal ions in the food industry, industrial waste, drinking water, and bodily fluids, such as blood and urine, is a very challenging problem. More sensitive and cost effective electrode materials that cause significantly less contamination are required to monitor the toxic elements in such media on a routine basis. Electrochemical methods require minimal sample preparation, and miniaturization of the test electrode can conveniently be achieved. Polarography has been successfully used to detect trace elements, antioxidants, organic compounds, vegetable oils, etc. in the food industry. The mercury electrode itself is a toxic material, but mercury liquid electrode material is very useful for simultaneous determination of more than one metal, such as Cu, Cd, Pb, and Zn in the solution during a single polarographic scan. It is possible to maintain a high degree of surface cleanliness using a dropping mercury electrode (DME), which is very important in electroanalytical chemistry. Diamond has a higher useable potential range in solutions than mercury. Diamond is the most inert material in strong acids, alkalis, and neutral solutions. Therefore, diamond may have a use in detecting heavy metal ions like lead, cadmium, silver, and copper in various solutions. Diamond electrodes exhibit a very low corrosion rate and a very low double layer capacitance in our earlier studies [2–11]. Identification of toxic elements such as lead, arsenic, selenium, zinc, cadmium, mercury, copper, manganese, chromium, silver (not toxic) and tellurium in drinking water and food stuff is a very important task. The presence of cadmium and lead in drinking water may cause pulmonary, gastroenteritis and cerebral edema, and peripheral nerve degeneration, respectively. Copper sulfate has wide use as an agricultural poison and as an algaecide in water purification.

When making measurements, the diamond electrode is first held at a positive or anodic potential at which either oxygen evolution or some other gas evolution occurs depending on the type of solution employed in the study. The potential applied to the electrode is scanned in the cathodic direction to reduce the metal ions present in the solution, and the resulting currents are measured. As the potential approaches the value at which each of the metals reduce, current begins to flow, eventually reaching a maximum. As the applied potential is further increased, depletion of the electroactive reactants, such as metal ions, and the formation of a concentration gradient leads to a decrease in current. If multiple

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electroactive species are present in the solution, several peaks will be seen independently or superimposed on a rising baseline current as the potential is shifted cathodically. The current peaks thus obtained correspond to the complete reduction of each metal ion species from the solution. By determining the total charge, or current corresponding to each peak, the concentration of each metal ion in the test solution can be computed typically using pre-calibration or serial additions of known reference concentrations. This technique may be very useful in applications such as trace heavy metal ion concentration measurements in water and soil, as well as general applications in analytical and clinical chemistry and other fields.

Differential pulse voltammetry (DPV) is a widely used quantitative electrochemical method for determining the concentration of reducible or oxidizable substances in solution. The method was developed as a way to eliminate, or greatly reduce, the effect of charging current relative to the faradaic current, and to express the signal in a more easily quantifiable form. In differential pulse voltammetry, a series of potential pulses of fixed but small amplitude are superimposed on a constant dc voltage ramp near the diamond electrode/solution interface. Two measurements are made for each pulse; one just before the pulse is applied, and one just before the end of the pulse, to yield the differential current value. The differential current will be reported against the applied potential to give the peak shaped voltammogram, which is equivalent to the experimentally obtained derivative of the sigmoidal normal pulse voltammogram. Differentiation of the signal largely eliminates the charging current, since the only charging current present in the signal after subtraction of the current obtained just prior to the pulse is that arising from the small pulse. Linear sweep voltammograms do not provide as convenient a peak shape for quantification. In DPV, ions that reduce at different potentials will show up as separate peaks if their reduction potentials are sufficiently different. The diamond electrode material is convenient to use, provides higher operating current, and, most importantly, avoids mercury based toxic sensor material. In case the peak shaped response was not observed during the forward DPV scan, the reverse DPV scan might reveal the peak shaped voltammetric feature corresponding to that metal ion around its calculated Nernst potential.

There have been some reports on the characterization of diamond films by electrochemical techniques. Ramesham *et al.* [12] have demonstrated the growth of polycrystalline diamond over glassy carbon and graphite electrode materials for various electroanalytical applications. A process for selective seeding of conducting molybdenum and copper substrates with submicron diamond particles has been reported by electroplating techniques in [13]. Swain and Ramesham [2], Swain [14], Martin *et al.* [15], Alehashem *et al.* [16] have reported the cyclic voltammetric behavior of ferri/ferrocyanide using boron-doped diamond films. Miller *et al.* [17] have reported the cyclic voltammetric behavior of ferri/ferrocyanide using cobalt ion implanted diamond electrodes. Vinokur *et al.* [18] have reported the effect of resistance, or boron doping level, in the CVD diamond film on the electron transfer kinetics of various redox couples. Ramesham *et al.* [4–11] have reported the electrochemical behavior of undoped diamond deposited by the hot-filament technique and the microwave plasma technique, as well as doped-diamond by microwave plasma CVD in 0.5 M NaCl solution using AC impedance and DC polarization techniques. Awada *et al.* [19] have studied the electrodeposition of metal adlayers of Pt, Pb, Cu, and Hg on the boron-doped diamond electrode material by cyclic voltammetry and square wave voltammetry to study the spatial reactivity of the electrode material. We have used differential pulse voltammetry and reverse differential pulse voltammetry to study the identification of the toxic heavy metallic ions like lead, cadmium, silver, and copper in various types of electrolyte solutions.

DPV is the most useful electroanalytical technique to study the electroactive species to evaluate an electrode surface. The test electrode (working electrode) plays a critical role in the electrochemical experiments. The working electrode is where the reactions of interest take place and are usually constructed of chemically inert material. This test electrode should have very low background current, wide potential limits for cathodic and anodic reactions, fast electron-transfer kinetics, low double capacitance, reproducibility of voltammetric response, and stability of electrode material itself in order to use in electroanalytical applications for long time. The diamond electrode material may have use in characterizing the pollutants in hazardous waste environments and detection of accidental metal contamination in a practical environment.

Good quality diamond films have been grown using less than 1% methane in hydrogen at a pressure of 30–40 Torr [4–11, 20–26]. Diamond films are chemically inert in a variety of environments including strong acidic, alkaline, fluoride and chloride environments and therefore might have a significant use in electroanalytical applications. Boron-doped diamond films are electrically conducting [4–11, 22] and therefore, differential pulse voltammetric and reverse differential pulse voltammetric behavior is of significant practical interest in the field of electroanalytical detection of toxic metallic ions.

2. Experimental details

Surface damaging is a necessary process to nucleate CVD diamond on non-diamond substrates. Ultrasonic agitation of the substrates was performed in methanol containing synthetic diamond particles of 60–90 μm typical size for 10 to 60 min and washed with tap water, acetone methanol, and deionized water [4–11, 20–26].

A microwave plasma (2.45 GHz) assisted CVD system (ASTeX, Woburn, MA) has been used to grow diamond films. A schematic diagram of the diamond deposition system has been described earlier [20–26]. The substrate was placed at the center of the stage that was then loaded into the quartz bell jar reactor. The reactor was evacuated to a base pressure of 10^{-4} Torr. A plasma was obtained by adjusting the pressure in the chamber, the hydrogen flow rate, microwave power, and wave guide tuning. The substrate was heated *in-situ* by the microwave plasma to attain the desired substrate temperature before initiating the growth of diamond. Ultra high purity grade hydrogen and research grade methane was used in our experiments. The temperature was monitored remotely by an optical pyrometer. Diamond deposition was started by injecting methane into the system when the substrate reached the desired temperature. The deposition rate under the typical microwave plasma operating conditions was normally $\sim 1\,\mu$m/h. A continuous film of diamond was usually obtained after 10 to 12 h of growth.

Boron doping of diamond film was achieved by using a solid disk source consisting of B_2O_3 and other oxides. The solid disk of boron source has been used as a base to the substrate during growth of *in-situ* doped diamond at a substrate temperature of $925 \pm 25\,^\circ$C. The size ($\sim$30 mm × 30 mm) of the boron source disk is greater than that of the substrate ($\sim$21 × 21 mm) where the source disk can be exposed to the hydrogen and methane microwave plasma which will raise the source disc's temperature ($\sim$1000 °C). This will allow sufficient vapor pressure of boron in the plasma at a diamond growth temperature to eventually result in an *in-situ* doping of diamond. Typical deposition parameters are provided in [21, 22].

All solutions were prepared using reagent grade chemicals in deionized water. Differential pulse voltammograms and reverse differential pulse voltammograms were obtained at a scan rate of 5 mV s^{-1} (pulse height: 25×10^{-3} V, pulse width: 50×10^{-3} s, scan increment: 2 mV, and step time: 0.4 s). The exposed area of the boron-doped diamond electrode is 0.71 cm^2. The reference electrodes of Ag |AgCl| 0.5 M NaCl and Hg $|Hg_2SO_4|$ (saturated K_2SO_4), have been used in the reported experiments. The potential of the reference electrode is 0.24 V and 0.615 V vs. SHE, respectively. A platinum foil counter electrode was used during all of the electrochemical measurements. All of the electrochemical experiments were conducted at room temperature ($\sim$25 °C). The solution was not purged and it could have been oxygen saturated during the electrochemical measurements. A simple three electrode (test electrode, counter electrode, reference electrode) electrochemical cell was used in this study. A potentiostat (EG & G Model 273) was used in our experiments to perform differential pulse voltammetry and reverse differential pulse voltammetry (EG & G Model 270 Research Electrochemistry Software package). We have not corrected the experimental data for uncompensated IR drop and subtracted for background current response. The solution was not stirred during the DPV and RDPV experiments. The boron-doped diamond electrode was cleaned with acetone, alcohol, and deionized water prior to the electrochemical experiments.

3. Results and discussion

Our preliminary study is to demonstrate the analytical utility of the synthetic boron-doped CVD diamond electrode that was tested in various electrolyte solutions contain lead, cadmium, silver, and copper ions by using differential pulse voltammetry and reverse differential pulse voltammetry.

Fig. 1a shows the background current response for the doped diamond electrode in 0.5 M NaCl solution at a scan rate of 5 mV/s. We have not observed any DPV peak corresponding to lead ion in a blank solution (0.5 M NaCl) employed in this study. Fig. 1b shows the differential pulse voltammogram for 1 mM Pb^{2+} ion concentration in 0.5 M NaCl solution at a scan rate of 5 mV/s using the boron-doped diamond as a test electrode. Table I shows the standard electromotive force potentials with respect to SHE at 25 °C for various test electrode ions along with toxic materials that have unit activity [27]. We have also provided the calculated Nernst potentials at various concentrations (assume the activity equal to the concentration for the sake of discussion). Lead deposition should occur at −0.214 V vs. SHE when the potential of diamond

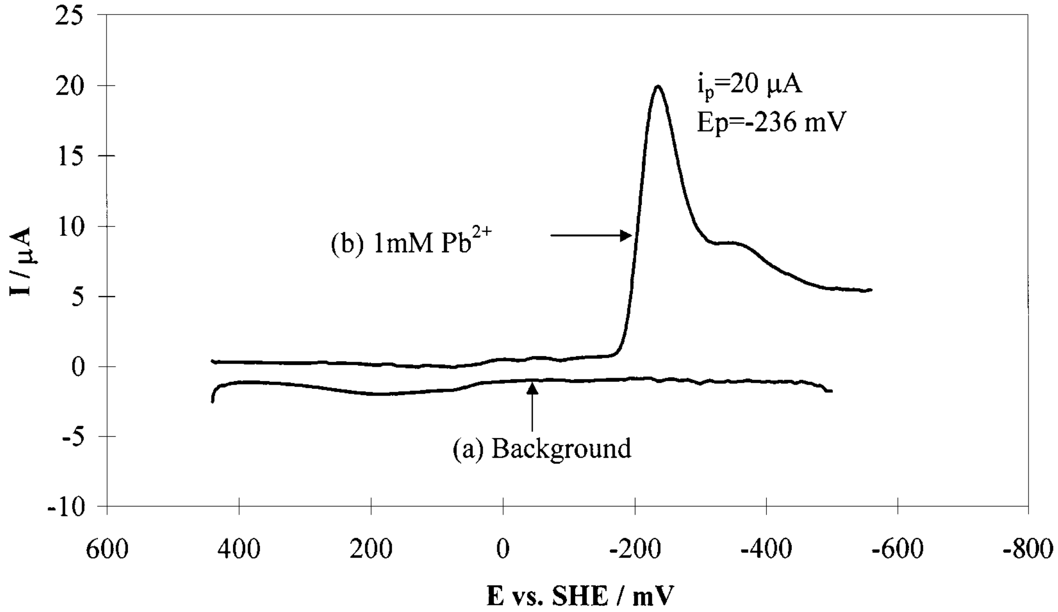

Figure 1 (a) Background differential pulse voltammogram for boron-doped diamond electrode in 0.5 M NaCl solution. (b) Differential pulse voltammogram for 1 mM Pb^{2+} ions in 0.5 M NaCl solution.

TABLE I Electromotive force potentials for reduction reaction [27]

Reduction reaction	E^0 (Reduction) (Unit activity)	E^a (1 mM)	E^a (3 mM)	E^a (5 mM)
$Au^{3+} + 3e^- \rightarrow Au$	+1.5			
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.229			
$Pt^{2+} + 2e^- \rightarrow Pt$	+1.2			
$Ag^+ + e^- \rightarrow Ag$	+0.799			
$2Hg_2^{2+} + 2e^- \rightarrow 2Hg$	+0.792			
$H_2SeO_3 + 4H^+ + 4e^- \rightarrow Se + 3H_2O$	+0.74			
$TeO_2 + 4H^+ \rightarrow Te + 2H_2O$	+0.53			
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.342	+0.253		
$HAsO_2 + 3H^+ + 3e^- \rightarrow As + 2H_2O$	+0.247			
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126	−0.214		
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23			
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.402	−0.49	−0.476	−0.47
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74			
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.763			

[a] $M^{n+} + ne^- \rightarrow M$
$E = E^0 + [0.059/n] \log(a^+_M)$.

electrode is scanned (forward) from anodic potential (+ve) to a more cathodic potential (−ve) when the activity of lead ions is 1 mM. The observed potential corresponding to a DPV peak in Fig. 1 is about −0.236 V vs. SHE. The detected peak for the lead ion is sharp and well defined which will help in determining the unknown concentration of lead unambiguously.

Fig. 2a shows the background current response for the doped diamond electrode in 0.5 M H_2SO_4 solution at a scan rate of 5 mV/s. We have not observed any DPV peak corresponding to cadmium ion in a blank solution used in this experimental study. Fig. 2b, c, and d shows the differential pulse voltammograms for 1, 3, and 5 mM Cd^{2+} ion concentration in 0.5 M H_2SO_4 solution at a scan rate of 5 mV/s using the boron-doped diamond as a test electrode material, respectively. Cadmium deposition should occur at −0.49 V, −0.476 V, −0.47 V vs. SHE when the potential of the diamond electrode is scanned from an anodic potential (+ve) to a more cathodic potential (−ve) when the activity of cadmium ions is 1, 3, and 5 mM, respectively. The observed potential corresponding to a DPV peak in Fig. 2 is about −0.640 V vs. SHE. The detected peaks for the cadmium ion is sharp and well defined and but deviated slightly from the predicted value. This may be due to the nucleation and electrochemical plating process during the scanning from positive to negative potential. Fig. 3 shows the cadmium ion concentration vs. the observed peak current demonstrates the linear relationship in the concentration range of cadmium ions studied. This plot may be used as a calibration curve to determine the concentration of unknown cadmium ion in various desired environments.

Fig. 4a shows the background current response for the doped diamond electrode in 0.5 M H_2SO_4 solution at a scan rate of 5 mV/s. We have not observed any DPV peak corresponding to copper ion in a blank solution used in this experimental study. Fig. 4b and c shows the differential pulse voltammogram (forward) and reverse differential pulse voltammogram for 1 mM Cu^{2+} ion concentration in 0.5 M H_2SO_4 solution at a scan rate of 5 mV/s using the boron-doped diamond as a test electrode material. Copper deposition should occur at +0.253 V vs. SHE when the potential of diamond electrode is scanned from anodic potential (+ve) to a more cathodic potential (−ve) when the activity of copper ions is 1 mM. We have not observed any characteristic peak corresponding to copper deposition during potential scanning from positive to negative. We have scanned the potential of the diamond electrode

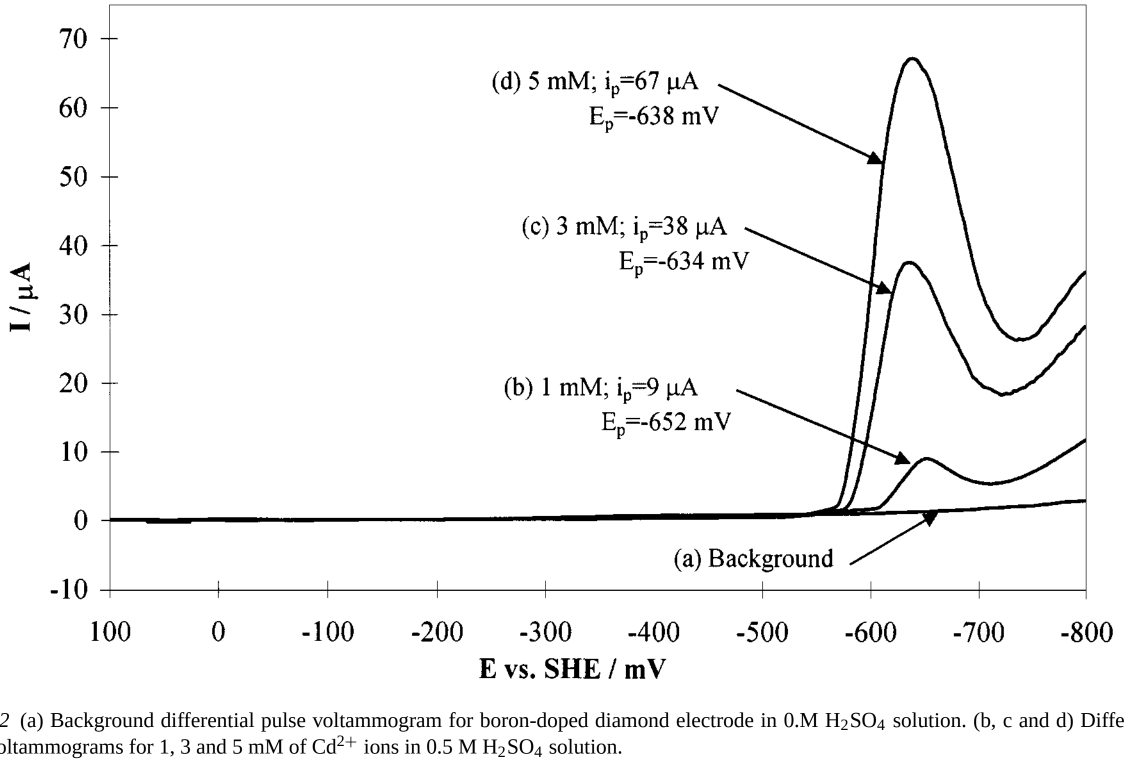

Figure 2 (a) Background differential pulse voltammogram for boron-doped diamond electrode in 0.M H_2SO_4 solution. (b, c and d) Differential pulse voltammograms for 1, 3 and 5 mM of Cd^{2+} ions in 0.5 M H_2SO_4 solution.

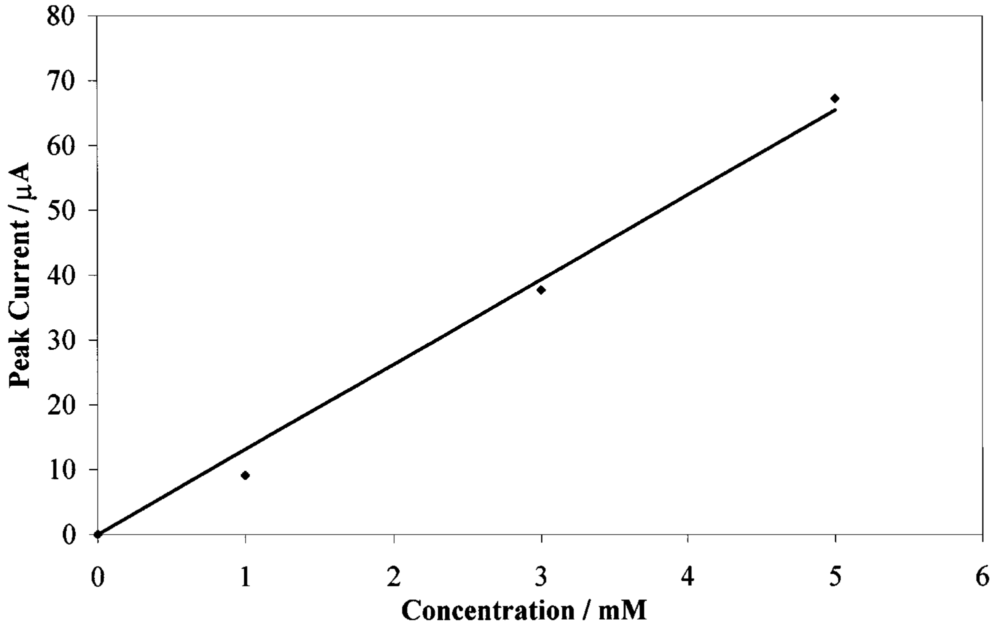

Figure 3 The observed peak current in Fig. 2b, c and d vs. concentration of Cd^{2+} in 0.5 M H_2SO_4 solution.

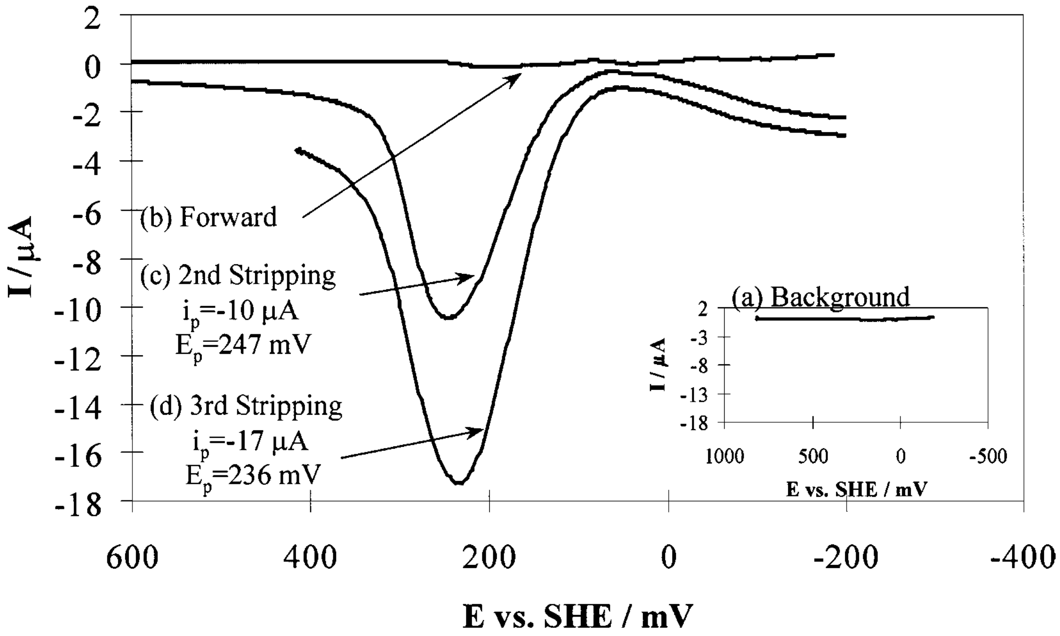

Figure 4 (a) Background differential pulse voltammogram for boron-doped diamond electrode in 0.5 M H_2SO_4 solution (inset). (b) Differential pulse voltammogram for 1 mM Cu^{2+} ions in 0.5 M H_2SO_4 solution. (c) Reverse differential pulse voltammogram obtained for a diamond electrode after the forward scan (positive to negative potential) where applied negative potential is lower in magnitude and shorter time than in (d).

from negative potential to positive potential (reverse) after the scan in Fig. 4b. We did observe the stripping of copper during reverse differential pulse voltammetry for copper deposited over diamond electrode during the forward scan. The observed potential corresponding to the peak (+0.236 to 0.247 V vs. SHE) matches with the value predicted (+0.243 V vs. SHE) as shown in Table I with a high degree. This may be due to more than one competitive possible reactions occur during forward scanning than reverse scanning. There could be hydrogen evolution, oxygen reduction, metal electroplating, etc. during forward scanning. There may be only stripping of electroplated copper during the reverse scan and there could be oxygen evolution reaction during extreme positive potentials. The negative potential should be constant in principle for all the concentrations studied. Otherwise, the peak current during the reverse scan depends on the magnitude of the negative potential during the forward scan and also the duration for which the negative potential was applied to the diamond electrode. It is critical to maintain constant negative potential and constant duration of applying such potential for stripping voltammetry studies. The observed potential corresponding to a RDPV peak in Fig. 4 is about +0.236 to 0.247 V vs. SHE. The detected peak for stripping of copper from the diamond electrode is sharp and well defined and correlates well with the predicted value. If the electrode is scanned to a high negative potential it may be possible that the diamond electrode may experience

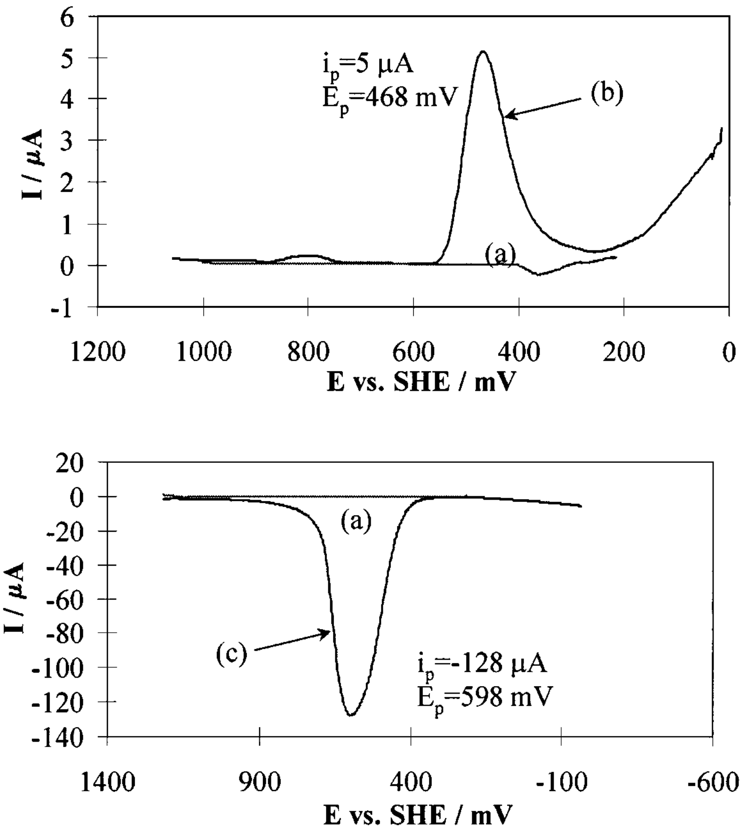

Figure 5 (a) Background differential pulse voltammogram for boron-doped diamond electrode in 0.5 M HNO_3 solution. (b) Differential pulse voltammogram for 1 mM Ag^+ ions in 0.5 M HNO_3 solution. (c) Reverse differential pulse voltammogram obtained for a diamond electrode after the forward scan.

hydrogen evolution reaction and that may erode the deposited toxic metal during the forward scan. This may yield a lower peak current during reverse differential pulse voltammetric studies. Fig. 4c and d demonstrates reverse differential pulse voltammograms where the diamond electrode has experienced different negative potentials during forward scan. Higher the negative potential during forward scans yielded lower peak current during reverse scans for stripping of the deposited metal.

Fig. 5a shows the background current response for the doped diamond electrode in 0.5 M HNO_3 solution at a scan rate of 5 mV/s. We have not observed any DPV peak corresponding to silver ion in a blank solution used in this experimental study. Fig. 5b and c shows the differential pulse voltammogram (forward) and reverse differential pulse voltammogram for 1 mM Ag^+ ion concentration in 0.5 M HNO_3 solution at a scan rate of 5 mV/s using the boron-doped diamond as a test electrode material. Silver deposition should occur at +0.6 V vs. SHE when the potential of diamond electrode is scanned from anodic potential (+ve) to a more cathodic potential (−ve) when the activity of silver ions is 1 mM. We have observed a mild characteristic peak corresponding to silver deposition during potential scanning from positive to negative. We have scanned the potential of the diamond electrode from negative potential to positive potential (reverse) after the scan in Fig. 5c. We did observe the stripping of silver during reverse differential pulse voltammetry for silver deposited over diamond electrode during the forward scan. The observed potential corresponding to the peak matches with the value predicted as shown in Table I with a very high degree. The observed potential corresponding to a RDPV peak in Fig. 5 is about +0.598 V vs. SHE. The detected peak for stripping of silver from the diamond electrode is sharp and well defined and correlates well with the predicted value.

In summary, we have demonstrated a versatile synthetic CVD boron-doped polycrystalline diamond electrode for the detection of toxic heavy metal ions by using differential pulse voltammetry and reverse differential pulse voltammetry in various electrolyte solutions. Metal ions that include lead, cadmium, copper, and silver were studied in this paper. The reversible potential for these metal ions varies from +0.799 to 0.4 V vs. SHE. This range is more than the range that could be studied by using mercury electrode. The diamond electrode may even be useful to detect gold and platinum in the solutions. The diamond electrode is chemically inert in strong acids and therefore can be used to detect the dissolved platinum and gold in aqua regia (1 part conc. HNO_3 and 3 parts conc. HCl) and hydrofluoric acid (HF) solutions. We have detected the presence of silver in the solution that may even suggest it is possible to detect the mercury ions in the solutions. Our future study is to fabricate microdiamond electrode to detect parts per billion level toxic metal ion concentration in various applications such as analytical, environmental, process monitoring, clinical analysis, under ground water analysis, contamination of organic compounds, acids, bases, neutral solutions, particularly strong acids, marine surveys, hostile environments, industrial quality control, hazardous waste sites, etc. The diamond technology may replace the need for mercury electrodes and offer a possibility to miniaturize the diamond electrode for electroanalytical detection of toxic metal ions. The microdiamond electrode may have a several advantages such as electrolyte stirring, toxic mercury electrode, performing the experiment in neutral gas ambient, adding a supporting electrolyte, is unnecessary to detect and evaluate the presence of toxic metal ions. We feel that the CVD diamond electrode may have a wide variety of useful applications to solve inherent analytical problems in electroanalytical and bioelectroanaltytical chemistry. This electrode could be used to detect simultaneously various metallic ions in the same solution over a wide potential range and this is a very significant result with respect to analytical applications in particular to plating industries to monitor the metallic ion concentrations as a function of its use. The diamond electrode may be useful to determine the thickness of various metallization layers that are quite routinely employed in the semiconductor industrial processes.

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