



# From micro to nanocrystalline boron doped diamond applied to cadmium detection



André F. Sardinha<sup>a,\*</sup>, Tatiane M. Arantes<sup>b</sup>, Fernando H. Cristovan<sup>c</sup>, Neidenei G. Ferreira<sup>a</sup>

<sup>a</sup> Instituto Nacional de Pesquisas Espaciais, Av. dos Astronautas 1758, São José dos Campos, SP, Brazil

<sup>b</sup> Instituto Federal Goiano, - Campus Rio Verde, Rod. Sul Goiana Km 01, Rio Verde, GO, Brazil

<sup>c</sup> Universidade Federal de São Paulo, Instituto de Ciência e Tecnologia, R. Talim 330, São José dos Campos, SP, Brazil

## ARTICLE INFO

### Article history:

Received 25 April 2016

Received in revised form 20 January 2017

Accepted 25 January 2017

Available online 26 January 2017

### Keywords:

Cadmium detection

Boron doped diamond

Heavy metals

Square wave anodic stripping voltammetry

## ABSTRACT

Cadmium detection was investigated by Square Wave Anodic Stripping Voltammetry (SWASV) measurements by using boron doped diamond electrodes with different morphologies from micro to nanocrystalline grains as Boron Doped Diamond (BDD) and Boron Doped Nanocrystalline Diamond (BDND), respectively. The argon concentrations, in the argon/hydrogen ratio, used were 0, 50, 60, 70, and 80 vol.%. SWASV technique was applied in  $4 \times 10^{-4}$  mol L<sup>-1</sup> ammonium acetate buffer pH 4.2. The peak currents were measured for Cd<sup>2+</sup> concentration ranging from 1 to 20 µg L<sup>-1</sup>. This change in film grain size and roughness affected how cadmium was deposited on the electrode surfaces, thus affecting its electroanalytical response from SWASV measurements as well as its selectivity. For all electrodes cadmium detection limits (DL) were lower than 1 µg L<sup>-1</sup> while for BDND electrode DL reached 0.016 µg L<sup>-1</sup>. These values are lower than that required by the Brazilian Health Ministry for potable water (1 µg L<sup>-1</sup>) and confirm that diamond electrodes are a suitable mercury-free method to determine cadmium trace levels in water. A strong correlation between the electrode selectivity and its grain size also confirmed the best performance of BDND electrode.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

Heavy metals, such as Cu, Zn, Cd, Hg, and Pb belong to the category of environmentally toxic substances and tend to accumulate in the human body. Cadmium is a particularly toxic substance that causes health and environmental effects because it is used in different industrial processes, including electroplating, paint pigmentations, and nickel-cadmium batteries [1]. Humans are exposed to cadmium mostly through plant-derived food. There is no safe margin of cadmium exposure. Therefore, there is a crucial need to lower human exposure to it. Cadmium produces a number of health problems and it is known as carcinogenic substance. Cadmium affects blood pressure, prostate function and testosterone levels, induces bone damage, and can affect renal and dopaminergic systems in children [2–5]. For these reasons, the European Union has recently banned the use of cadmium in several types of electronic equipment through the issue of the “Restriction on Hazardous Substances” directive (RoHS) [6]. Thus, the maximum contaminant level of cadmium in water allowed by US Environmental Agency is 5 µg L<sup>-1</sup> [7]. In Brazil, according to the CONAMA resolution no. 357 [8], the maximum value of cadmium for wastewater is 200 µg L<sup>-1</sup> whereas

the Ordinance no. 2914 of Brazilian Health Ministry allows 5 µg L<sup>-1</sup> for potable water [9].

The spectroscopic methods are the most useful for these levels of cadmium detection and require expensive equipments as well as complex analyses. An alternative methodology for metal traces detection is the Anodic Stripping Voltammetry (ASV) which presents simplicity of instrumentation and faster result analyses when compared to those for spectroscopic measurements. In the past, polarography with mercury electrode was largely used for electroanalytical detection [10]. However, nowadays it is highly recommended the use of other kinds of materials with low or null toxicity. In this context, boron doped diamond (BDD) films appear as a new technological material with singular properties [11,12]. The BDD is resistant to fouling and can be reused many times, also due to its chemical inertness and mechanical robustness for corrosive media [13].

These properties have favored the evolution to use diamond to detect a variety of analytes, including heavy metals traces as well as pesticide determinations substituting the mercury electrodes in analytical techniques [14–16]. Taking into account BDD film properties, the production of boron doped nanocrystalline diamond (BDND) may result in the electroactive area increase due to the diamond grain size decrease promoting its analytical sensitivity and selectivity increase [17,18]. Considering the electrochemical characteristics of sensors based on BDND, several studies have reported promising results for these electrodes

\* Corresponding author.

E-mail address: [andresardinha2@hotmail.com](mailto:andresardinha2@hotmail.com) (A.F. Sardinha).

like a fast response, low detection limit, high stability, and excellent response accuracy [19–22]. In addition, nanocrystalline films provide a better catalytic activity, decreasing the overpotential of certain oxidation-reduction reactions [23].

Some studies have demonstrated the importance of BDND electrodes. May et al. [24] have studied the relationship among the film morphology, conductivity, and boron doping level. They suggested that the production of electrodes with controlled roughness and conductivity can make them excellent candidates for electrochemical applications. Sonthalia et al. [25] have compared the BDND electrodes with mercury electrodes for the detection and quantification of Ag(I), Cu(II), Pb(II), Cd(II) and Zn(II) in several samples of water. They concluded that the diamond electrode has the same properties as those of the mercury electrode without toxicity in addition to its chemical inertia and its non-volatility. More recently, G.G. Honório et al. [26] have used BDD to determine metal traces in honey by differential pulse anodic stripping voltammetry. They concluded that pre-cathodically treated electrode showed more reliable results. In addition, L. Pujol et al. [27] have published a systematic review article pointing out the electrochemical sensors and devices for heavy metals assay in water. Among different electrode materials, they discussed that BDD electrodes are very reproducible in all measurements, independently of their aging not to mention their known singular properties.

Many electroanalytical methods employ the adsorptive accumulation at the hanging mercury drop electrode (HMDE) combined with different stripping voltammetric techniques. One of the most sensitive techniques is the square-wave voltammetry (SWV), which is considered a powerful electrochemical technique and may be applied to both electrokinetic and analytical measurements [28,29]. Its detection limits can be compared with those of chromatographic and spectroscopic techniques [30–32]. Furthermore, the analysis of the characteristic parameters of this technique also enables the mechanism and kinetic evaluation of electrochemical process under study. Thus, SWV allows analyzing the reversible, irreversible and quasi-reversible electrode reactions considering the correlations among the parameters such as frequency, step potential, and amplitude of the square wave [30–32].

Concerning cadmium detection, Pujol et al. have published a review, considering French researcher contributions, for electrochemical sensors and electroanalytical methods, within the last 20 years. They showed a Table describing analytical performances and experimental conditions obtained for heavy metal detections [27]. More recently, Zhang et al. have studied Cd<sup>2+</sup> determination using ultrasound-assisted square wave anodic stripping voltammetry and have compared their results with other anodic stripping techniques at BDD electrode [33]. Thus, we also added a survey with some important published results related to cadmium detection limit (DL) determination from electrochemical techniques (Table 1 [1,33–36]) as well as from spectroscopic techniques (Table 2 [37–40]). Feldman et al. have discussed that although the spectroscopic methods have good selectivity and high sensitivity for heavy metal detections, they present high operation and maintenance costs. Besides, they need to be associated with other extraction and separation techniques [41]. On the other hand, the electrochemical methods are an interesting alternative due to the advantage of easier experimental procedures with lower

**Table 1**  
Cd<sup>2+</sup> determination from electrochemical ASV techniques.

Electrode's Material	DL	References
Silver	1 nM	[34]
Tantalum	0.57 ppb	[33]
Bismuth film on glassy carbon	0.1 ppb	[33]
Bismuth film on carbon fiber	0.3 ppb	[33]
Boron doped diamond	1 ppb	[35]
Boron doped diamond	10 ppb	[1]
Mercury film on glassy carbon	5 pM	[36]

**Table 2**  
Cd<sup>2+</sup> determination from spectroscopic techniques.

Method	DL (ppb)	References
Atomic Absorption Spectroscopy (AAS)	0.0014	[37]
Atomic Absorption Spectroscopy (AAS)	0.003	[38]
Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)	10	[39]
Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES)	0.1	[40]

maintenance and operation costs compared to those of spectroscopic methodologies not to mention their fast analyses [42].

In a previous paper, we studied the lead detection using four types of BDD and BDND electrodes also considering the doping level variation [43]. By continuing our investigation, this paper aims the possibility of achieving film morphologies from BDD to BDND by increasing the argon concentration in the growth gas mixture (Ar/CH<sub>4</sub>/H<sub>2</sub>) keeping the boron addition constant during the film growth process. Thus, five different morphologies of diamond films were produced and characterized. In addition, we studied their application to cadmium detection in ultra pure synthetic electrolytes using Square Wave Anodic Stripping Voltammetry (SWASV) technique. For this purpose, a thorough study was conducted using diamond electrodes with different morphologies considering the Cd stripping response as a function of their grain sizes. The voltammetric parameters were optimized for all electrodes studied, according to the methodology described in reference [43], taking into account the following results: (1) SWV curves for the net current (I), its forward (I<sub>f</sub>) and its backward (I<sub>b</sub>) components, (2) the dependence of the net peak current of reversible reaction as a function of the frequency square-root, (3) the dependence of the net peak current (I) and the net peak current /peak current width at half-height ratio (I/ΔE<sub>p/2</sub>) as a function of the square wave amplitude (E<sub>sw</sub>), and (4) the dependence of the net peak current (I) as a function of the step potential (E<sub>s</sub>). We also conducted the investigations to determine the best potential to be used in the Cd<sup>2+</sup> deposition step for each electrode surface. After these parameter optimizations for Cd<sup>2+</sup> system, the analytical curves were obtained in pure electrolyte by the standard addition method.

For analytical measurements DL represents an important parameter, which is defined as the smallest concentration or absolute amount of analyte present in the solution that can be detected with statistical confidence, but not quantified. Besides, DL signal is significantly larger than the signal arising from the electrolyte (blank signal). DL is calculated according the Eq. (1):

$$DL = 3 s/m \quad (1)$$

where *s* is the standard deviation for voltammetric measurements using the electrolyte and *m* is the arithmetic media these measurements [42,44]. Quantification limit (QL) can also be evaluated and it is defined as the lowest analyte concentration which can be quantitatively determined [44].

## 2. Experimental

Five film sets from BDD to BDND were produced in a Hot Filament Chemical Vapor Deposition (HFCVD) technique on Si substrate. Each film set with four samples were grown at temperatures from 900 to 1100 K. The reactor pressure was 4.0 kPa for deposition time of 16 h using the total gas flow of 200 sccm. The CH<sub>4</sub> concentration was kept constant in 1.0 vol.% and the Ar/H<sub>2</sub> was adjusted by varying the Ar concentration from 0 vol.% for BDD to 80 vol.% for BDND in the mixture, respectively. Five tungsten filaments were used keeping their temperature of around 2300 K. All films were grown on polished silicon (100) 1 × 1 cm<sup>2</sup> substrates prepared by ultrasonic hexane bath with 0.25 μm diamond powder during 60 min. Boron was obtained from an

Download English Version:

<https://daneshyari.com/en/article/5466328>

Download Persian Version:

<https://daneshyari.com/article/5466328>

[Daneshyari.com](https://daneshyari.com)