Titanium oxide electrodeposition on diamond/Ti electrodes with different boron dopings

A.B. Couto, F.L. Migliorini, M.R. Baldan, N.G. Ferreira

Instituto Nacional de Pesquisas Espaciais, São José dos Campos, Brasil.

The eletrodeposition of titanium oxide on semiconducting boron doped diamond grown on Ti substrate was investigated. Emphasis is given in the study of the influence of the doping level on BDD in the anodic hydrolysis of $TiCl_3$ for obtaining TiO_2/BDD composites. The BDD films as-grown were characterized by Raman Spectroscopy and the acceptor concentrations were evaluated around 10^{19} and 10^{21} boron atoms cm^{-3} for the electrode E1 and the electrode E2, respectively. Scanning electron microscopy showed that the deposits resulted in morphology composed of small grains distributed throughout the BDD surface for both electrodes. The influence of doping level showed that for E2 electrode, the deposits presented higher density with clusters at the grain faces and best uniformity of TiO_2 on its surface than that for E1 electrode. This behavior may be associated to the better conductivity of the electrode E2 due to its higher boron content enhancing the titanium oxidation reaction. According the X-ray diffraction data, the rutile TiO_2 crystallographic form was obtained for all the depositions.

Introduction

The photocatalytic processes is very well known as an excellent method for environmental and energy-supply related problems. This method consists in the acceleration of a chemical reaction by the presence of a semiconductor photoabsorber [1]. Among the semiconductors commonly used, titanium dioxide (TiO_2) is the most useful material for photocatalytic purposes due to its stability, non-toxicity and low cost [2]. It is noteworthy that its photocatalytic performance depends of the diverse factors like the size, pore volume, crystalline phase and the exposed surface faces. Thus, there is a large interest to development suitable material associated to adjusting these factors in order to improve the photocatalysis research. Fujishima and Honda [3] were the pioneering researchers to investigated titanium photocatalysis effect. They reported that it was possible to water splitting by means of a photoelectrochemical cell comprising of an inert cathode and a rutile titanium anode. Thenceforward, the titanium photocatalysis process to environmental applications has attracted more interest, especially on advanced oxidation processes for the destruction of organic species in wastewater [4, 5]. On the other hand, boron doped diamond (BDD) is a p-type semiconductor and this characteristics depends on the boron doping level. Due to its extremely wide gap (5.5 eV) and to the fact that the conduction band edge of the semiconductor p-type diamond is located at a very negative potential (-4.27 V versus SHE in 0.1 mol l^{-1} KH_2PO_4, pH=4.5),

its photoactivity can be exploited both by the photogenerated electrons in its conduction band reducing species that are very difficult to reduce under normal conditions[6] and by decomposition of organic and inorganic substances from contaminated water [7, 8]. Moreover, BDD have singular electrochemical properties, such as, wide potential window, low background current and extreme physical and chemical stability, which makes them appear as a solid electrode for application in electroanalysis and electrosynthesis [9, 10].

In this sense, the TiO_2/BDD composite systems are very interesting for generating both cathodic and anodic photocurrents. Thus, the goal of this work was to study the influence of the doping level on BDD in the anodic hydrolysis of $TiCl_3$ for obtaining TiO_2/BDD composites, with the intention of using them for photoelectrocatalytic applications.

Experimental Procedure

The BDD electrode was grown on Ti substrate by the hot filament chemical vapor deposition (HFCVD) technique. The deposition of diamond on titanium has a singular characteristic attributed to the strong stress formation between the film and the substrate, which arises from extrinsic and intrinsic factors. As a consequence, some pre- treatments on the substrate surface are required to decrease the stress and to increase the nucleation rate [11, 12].The mechanical incision is effective to increase the titanium surface area and roughness besides improving the mechanical anchoring of the film. This incision can be obtained in air abrasion with glass beads, or by scratching the surface with an abrasive agent as the diamond paste. In this work, the films were deposited on the titanium substrate after pre-treatment in air abrasion with glass beads. The BDD/Ti electrodes with the dimensions of 10 mm x 10 mm x 0.5 mm were prepared from methane hydrogen gas mixture with a pressure of 40 Torr and temperature around 650ºC, during 24 h. Boron source was obtained by an additional hydrogen line passing through a bubbler containing B_2O_3 dissolved in methanol with a controlled B/C ratio that permitted to produce films with different doping levels (10^{19} and 10^{21} atoms.cm^{-3}, denominated E1 and E2 respectively), estimated from Raman's measurements. All the electrochemical experiments were performed in a conventional three-electrode glass cell, using a platinum wire as a counter electrode and Ag/AgCl/$KCl_{(sat)}$ as the reference electrode. The TiO_2 electrodeposition on BDD films was performed under potentiostatic mode, at a fixed potential of 0.6 V during 10 min in a 50 mmol L^{-1} $TiCl_3$ (pH=2) + 0.1 mol L^{-1} KCl aqueous solution. The TiO_2 modified diamond films morphology was verified from the scanning electron microscopy (SEM) images using a Jeol JSM-5310 microscope and the X-ray Diffraction (XRD) patterns using a PANanalytical model X'Pert Powder diffractometer with the CuKα (λ = 1.54 Å), set at 45 kV and 25 mA, running in the ω/2θ scanning mode with ω = 1° and 2θ = 10 to 100°.

Results and discussion

Figure 1 shows the Raman´s scattering spectra of the E1 and E2 BDD films. The peak close to 1332 cm^{-1} corresponds to the vibration of a diamond first-order phonon, confirmed the quality of these BDD films. This peak decreased in intensity due to boron incorporation in diamond films. The effect of boron doping is reflected in the spectral features. There is the appearance of the two bands located at 500 cm^{-1} and 1220 cm^{-1} attributed to B-B vibrations and B-C vibrations, respectively [13]. The boron

concentration in diamond film was estimated from the fitting of 500 cm^{-1} peak using a combination of Gaussian and Lorenzian lines [14]. The acceptor concentrations were evaluated around 10^{19} and 10^{21} boron atoms cm^{-3} for the electrode E1 and the electrode E2 electrodes, respectively. The highest doping level of the electrode E2 is clearly observed in Figure 1 where the band at 1220 cm^{-1} is higher than that of the diamond peak not to mention its evident second order feature at around 2500 cm^{-1}.

The top view SEM image (not shown) of the diamond film deposited on the Ti substrates shows that the BDD film grew with a continuous and uniform surface morphology covering the whole substrate without delamination or cracks, characterized by well-shaped microcrystalline grains. It presents sharp facets and crystallographic orientation varying between <111> and <100>.
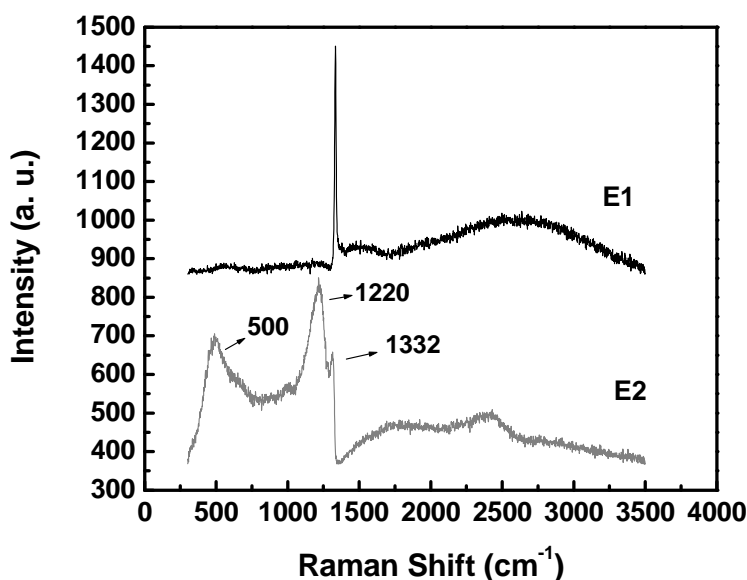

Figure 1: Raman spectra of E1 and E2 BDD electrodes.

The as-grown electrodes were used for all the electrochemical experiments performed in this work. To characterize the nature of the BDD electrodes as well as the deposit obtained, cyclic voltametry (CV) was carried out in 0.1 mol L^{-1} KCl containing 1.0 mmol L^{-1} K$_4$Fe(CN)$_6$ before and after electrodeposition of TiO$_2$ for E2 BDD electrode, presented in the Figure 2. The behavior of the E1 BDD electrode was similar (not shown).
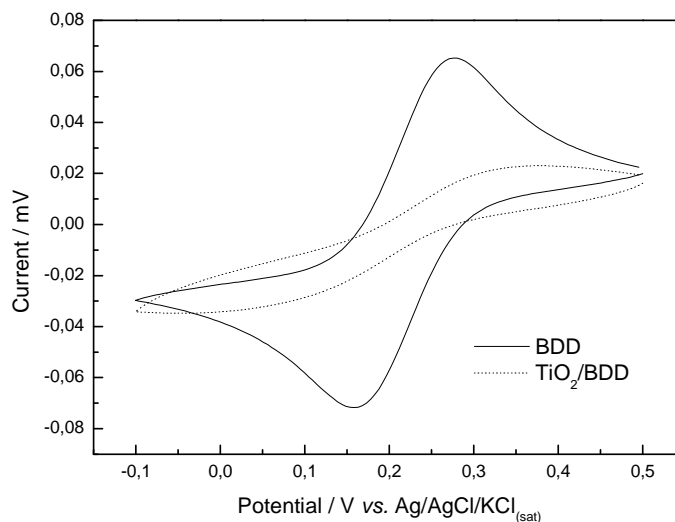
Figure 2: Cyclic voltammograms for E2 BDD electrode before and after TiO_2 electrodeposition, using 0.1 mol L^{-1} KCl + 1.0 mmol L^{-1} $K_4Fe(CN)_6$. Scan rate: 50 mV s^{-1}.

It is known that the presence of TiO_2 on the electrode strongly hinders inner-sphere electrochemical reactions [15]. It was observed in the Figure 2 a suppression of the oxidation and reduction peaks. This behavior is in strict accordance to the presence of oxide surface on the BDD, which confirms the presence of electrodeposited TiO_2 in both electrodes.

The Figure 3 shows the SEM micrographs of E1 and E2 electrode before and after surface modification of TiO_2 particles. These deposits resulting in morphology composed of small grains distributed throughout the BDD surface for both electrodes. From the anodic charge of Ti(III) oxidation, Q_a, and assuming that the composition of electrodeposited composite is TiO_2, the mass of the deposit was calculated:

$$m = 1/F \times M \times Q_a$$

(F is the Faraday constant and M the molar mass of TiO_2).

The amount of TiO_2 deposited on the E1 film was found to be 0.058 μg cm^{-2} while for the E2 film was 0.12 μg cm^{-2}. The E2 electrode exhibits the highest density with appearance of clusters at the grain faces and best homogeneity of TiO_2 on the electrode surface, while for the E1 electrode the electrodeposits presents low particle density. This morphological difference between two electrodes, concerning the homogeneity and the TiO_2 deposit densities, can be attributed to the better conductivity of the electrode E2 due to its higher boron content.
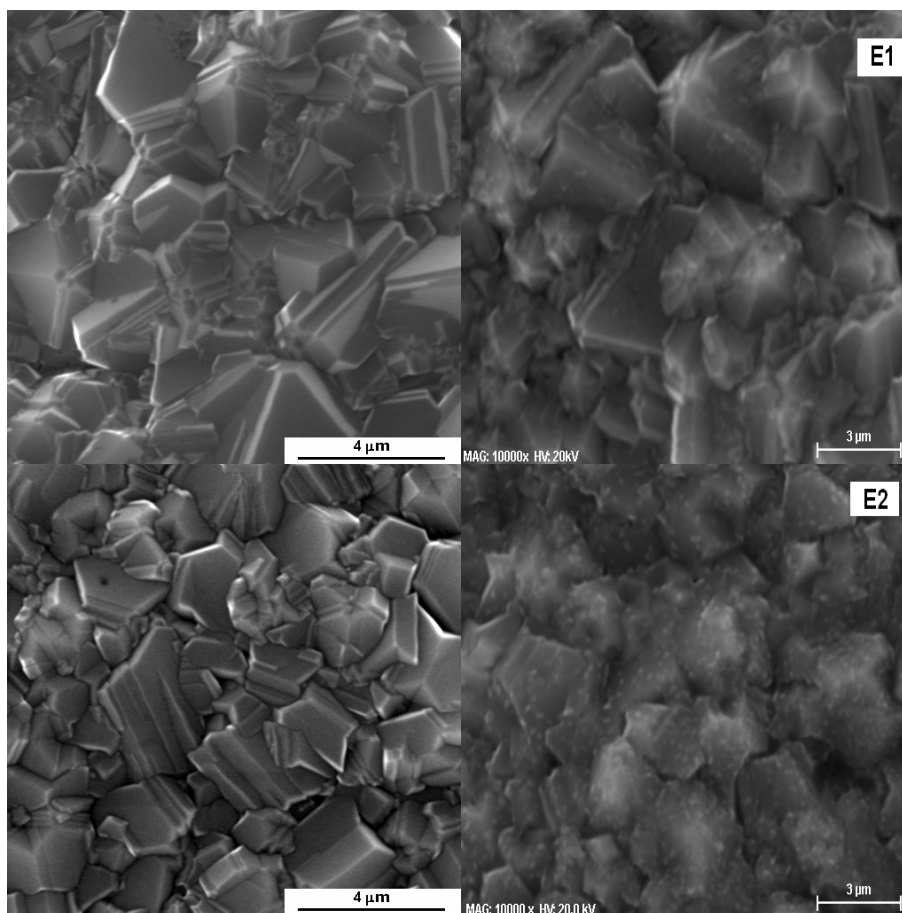
Figure 3: SEM images of E1 and E2 electrode before and after TiO$_2$ electrodeposits.

Figure 4 presents the X-ray diffraction measurements of the TiO$_2$ deposited on E1 and E2 electrode. According to the graphs, the rutile TiO$_2$ crystallographic form was obtained for all the depositions.
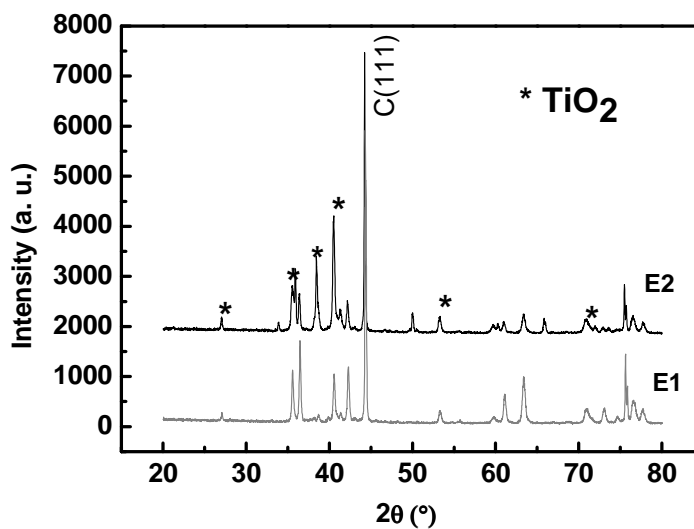

Figure 4: X-ray diffraction of E1 and E2 electrode after the TiO$_2$ electrodeposition.

Conclusion

This study showed that the TiO_2 electrodeposition process on semiconducting diamond surface can be a good alternative for the preparation of modified electrode at different doping levels. The TiO_2 electrodeposits presented morphology composed of small grains distributed all over the diamond crystal faces for both electrodes. The rutile TiO_2 crystallographic form was obtained for all the depositions. The SEM images showed a high density and homogeneity of TiO_2 electrodeposits for highly doped BDD electrode whereas for slightly doped BDD electrode the deposits presented low particle density. This behavior was attributed to the boron amount in this electrode, where the conductivity is better and, consequently, ensured an increase in the density of TiO_2 deposits.

Acknowledgments

References

[1] W.A. Zeltner, D.T. Tompkin, Ashrae Trans. 111 (2005) 532-534.
[2] K. Nakata, A. Fujishima, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 13 (2012) 169-189.
[3] A. Fujishima, K. Honda, Nature 238 (1972) 37-38.
[4] U. I. Gaya, A. H. Abdullah, Journal of Photochemistry and Photobiology C: Photochemistry Reviews 9 (2008) 1–12.
[5] A. Di Paola, E. García-López, G. Marcì, L. Palmisano, Journal of Hazardous Materials 211– 212 (2012) 3– 29.
[6] P. Muret, C. Saby, Semiconductor Science and Technology 19, (2004) 1-7.
[7] S. Yoshihara, K. Shinozaki, T. Shirakashi, K. Hashimoto, D.A. Tryk, A. Fujishima, Electrochimica Acta, 44 (1999) 2711-2719.
[8] C. Zhang, L. Gu, Y. Lin, Journal of Photochemistry and Photobiology A 207 (2009) 66- 72.
[9] M. Panizza, E. Brillas and C. Comninellis, Journal of Environmental Engineering and Management 18(3) (2008) 139-153.
[10] H. Sun, L. Dong, H. Yu and M. Huo, Russian Journal of Electrochemistry, 49 (2013) 883-887.
[11] S.J. Askari, F. Akhtar, G.C. Chen, Q. He, F.Y. Wang, X.M. Meng, F.X. Lu, Materials Letters 61 (2007) 2139-2142.
[12] A.F. Azevedo, E.J. Corat, N.F. Leite, V.J. Trava-Airoldi, Diamond Related Materials 11 (2002) 550-554.
[13] Li Niu, Jia-Qi Zhu, Xiao Han, Man-Lin Tan, Wei Gao, Shan-Yi Du, Physics Letter A 373 (2009) 2494-24500.
[14] M. Bernard, A. Deneuville, P. Muret, Diamond Related Materials 13 (2004) 282-286.
[15] A. Manivannan, N. Spataru, K. Arihara, A. Fujishima, Electrochem. Solid-State Lett. 8 (2005) C138-C140.