

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 – INPE
Av. Dos Astronautas, 1758, São José dos Campos, Brazil

abcouto@yahoo.com.br

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. 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 [1]. On the other hand, boron doped diamond (BDD) is a p-type semiconductor and this characteristics depends on the boron doping level. 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. 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. BDD films were grown by hot filament-assisted chemical vapor deposition technique on the titanium substrate, activated by methane hydrogen gas mixture with a pressure of 40 Torr and temperature around 650°C , 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 led to films with different doping level (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 $\text{Ag}/\text{AgCl}/\text{KCl}_{(\text{sat})}$ 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 3 and 10 min in a 50 mmol L^{-1} TiCl_3 (pH=2) aqueous solution. For preliminary photoelectrochemical tests, the light source was a deuterium lamp. The Figure 1 shows the Raman's scattering spectra of the E1 and E2 BDD films.

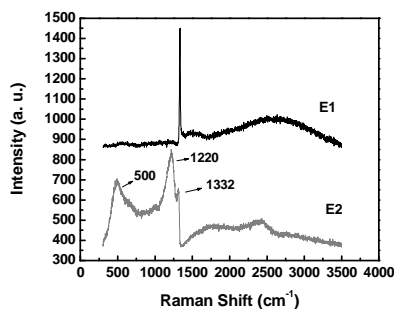


Figure 1: Raman spectra of E1 and E2 BDD electrodes.

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. The Figure 2 shows the surface modification of TiO_2 particles resulting in morphology composed of small grains distributed throughout the BDD surface. 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.

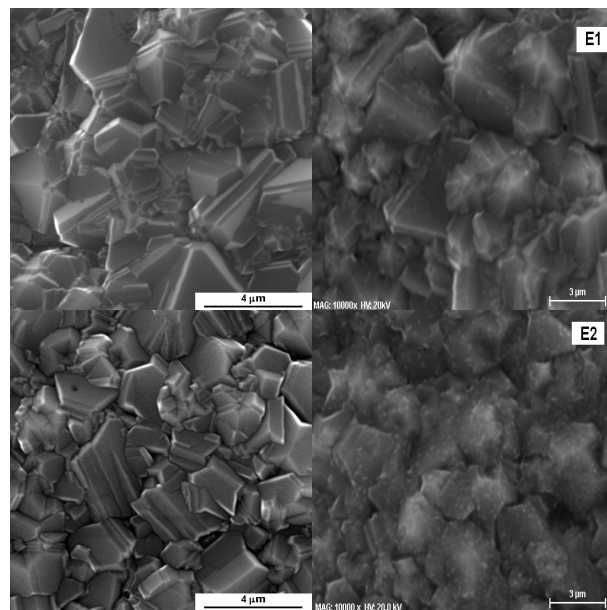


Figure 2: SEM images of E1 and E2 electrode before and after TiO_2 electrodeposits.

The X-ray diffraction measurements showed rutile TiO_2 crystallographic forms for all the depositions (Figure 3).

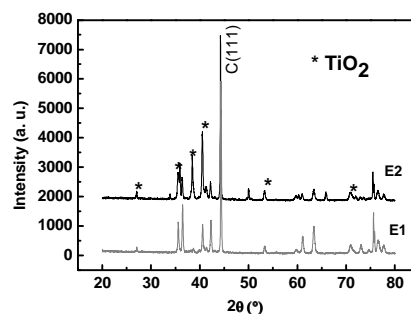


Figure 3: X-ray diffraction of E1 and E2 electrode after the TiO_2 electrodeposition.

The photoelectrochemical activity represented by n-type semiconductor (TiO_2) associated to the p-type semiconductor (BDD) was observed. It appears that this composite is worthy of development by exhibiting promises features to use as electrode in the electrooxidation of organic compounds in waters.

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References

[1] T. Spataru, M. Marcu, N. Spataru, Applied Surface Science, 269, 2013.