

Growth of Pt Clusters Electrodeposited onto Boron-Doped
Diamond Films

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The objective of this study is to obtain more insight on the number and the position of sites which are the most active in the electrochemical processes. This has a wide interest because the polycrystalline, boron-doped diamond (BDD) thin films have been recently used for a variety of electrochemical applications including metal recovery [1] and the oxidizing of the various organic residues [1, 2] contained in industrial waste waters. The activity of electrodes having a boron concentration range from $8 \cdot 10^{17}$ to $9 \cdot 10^{21} \text{ B.cm}^{-3}$ was found [3] to be mainly controlled by their doping level and more precisely by the occurrence and behaviour of their impurity band, which could supply either electrons or holes to the electrolyte through hopping between their electronic levels. However, despite of the large number of characterization methods used to study (microscopy, X-ray analysis, Raman & Auger spectroscopy, SIMS, cyclic voltammetry) various BDD films, nothing is yet clear about the number of the most active sites. Or, a higher number of diamond sites may lead to more efficient electrochemical processes occurring at a lower charge density and the increase of them can save an amount of electrical power.

Our hope is that the information reached from the cyclic voltammetry I/E profiles and the local probe microscopy (AFM, STM) images concerning the growth of electrodeposited Pt clusters could lead to more insight, both at the macroscopic and the microscopic scales, about the number and the position of the most active BDD sites.

EXPERIMENTAL

Several small sheets (10x25 mm) of BDD films grown via the hot filament chemical deposition technique (HF CVD) onto conductive silicon wafers have been treated under cycling at 100 mVs^{-1} scan rate during 4 hours in order to convert the hydrogen terminated surface to an oxygen-termination. Next, these samples have been immersed into a solution of 5 g/L H_2PtCl_6 contained in a small electrolytic cell (30 ml) and various potential sequences (fixed cathodic potential or several cycles at a rate of 50 mVs^{-1}) have been applied by using a three-electrode set-up in order to obtain low, medium or high Pt coverage. The I/E profiles of SiBDD/Pt were recorded in a second cell filled out with 0.1 M H_2SO_4 by using a conventional equipment. The morphology of the SiBDD/Pt deposits made on the anodically treated SiBDD has been examined in air by atomic force microscopy with a Nanoscope III instrument.

RESULTS AND DISCUSSION

Diamond micro-crystals, having facets mainly [111] oriented with some [100] orientation, the size of which varies from 0.2 to 0.7 microns, are seen on AFM or SEM images on the most examined samples. The deposit of Pt particles do not seem to be related to the geometrical characteristics of BDD crystals such as terraces or steps and some of the BDD crystals have no AFM observable Pt particles on them. A very small number of large Pt particles are observed at low Pt coverage but their number increases at medium and high Pt coverage. On the AFM images, the diameter of Pt particles can be precisely estimated as well as their height: a raft-like shape was found for most of them. However, for a more precise estimation of clusters sizes and heights, only $5 \times 5 \text{ nm}^2$ AFM images have to be used. In the case of a medium and a high Pt coverage, the histogram obtained for 68 Pt clusters display a maximum for heights around 140 nm and an average size of 449 nm. Thus, an ellipsoidal form can be reasonably attributed to the model average Pt cluster. Unfortunately, small Pt particles are hardly observed on the relatively large AFM windows needed for a systematic evaluation of sizes and heights of large Pt clusters, but can be only observed on narrow AFM windows which in contrast

are not so convenient for a statistic study. We therefore need information at a macroscopic scale, obtained by using voltammetry.

The I/E profiles recorded for each SiBDD/Pt sample at a scan rate of 50 mVs^{-1} in the potential range between 0 and 1.4 V (vs. a normal hydrogen electrode, NHE) display the characteristic peaks of polycrystalline Pt electrodes. From the amount of electricity corresponding to these peaks, due to the desorption of oxygen species and respectively to the adsorption/desorption of atomic hydrogen at Pt surface, the active surface of Pt deposits can be evaluate. The values of active Pt surface obtained from I-E measurements made at the macroscopic scale for the whole electrode area can be compared to those resulting from AFM (air, tapping mode) measurements made at the micron scale. The surface area of Pt clusters and particles (10.7 nm^2) found from the AFM images for the examined AFM window (141 nm^2) is much smaller than the surface of Pt deposits (6.1 cm^2) deducted from I-E profiles for the geometrical area examined (3 cm^2) of the same sample. This discrepancy can be understood because in both cases of medium or high Pt coverage, on the recorded AFM images can be seen not only large Pt particles observed at $5 \times 5 \text{ nm}^2$ AFM window, but also much smaller Pt particles observed only on a $0.7 \times 0.7 \text{ nm}^2$ AFM window. This clearly shows that the electro-deposition of Pt on the SiBDD surface preferentially occurs at some specific diamond sites. The preferential electro-deposition of Pt may be due to the boron doping which can be quite different from site to site at the microscopic scale. Such behaviour may result from the high electrical conductivity near some sites, presumably due to a higher local concentration of boron used in the BDD films as doping centres.

In conclusion, the morphological study of the electro-deposited Pt clusters and particles onto boron-doped diamond thin films has evidenced the presence of a limited number of BDD sites onto which the electrochemical processes preferentially occur. The increase of the number of such sites may have a great importance for the use of BDD electrodes in a variety of applications such as waste water treatment involving a large amount of consumed electricity.

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