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Effect of growth temperature on the electrodeposition of zinc oxide layers on diamond surfaces

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ABSTRACT

The electrochemical deposition of ZnO layers from an oxygenated zinc chloride bath has been realized on Boron Doped Diamond films as substrate for the first time. The influence of the bath temperature has been investigated from 20 °C to 80 °C. Scanning Electron Microscopy, X-Ray Diffraction and X-Ray Photoelectron Spectroscopy, performed on the treated surfaces, show the influence of the bath temperature on the composition, the structure and the morphology of the resulting deposits. For experiments made at 20 °C, a thin and non-covering amorphous layer constituted of $Zn(OH)_2$ is evidenced at the diamond surface. For deposits performed at bath temperatures equal or above 40 °C, the diamond electrodes are covered with a few μm thick ZnO layer. However, X-Ray Photoelectron Spectroscopy analysis suggests the additional presence of $Zn(OH)_2$ at the top surface of the zinc oxide deposits. The morphology and the crystallinity of these 2-D layers depend on the bath temperature. At 40 °C, the film is constituted of big and smooth micrometric grains, while at 60 °C the electrode is covered with closely packed and well crystallized ZnO micrometric rods. Finally, for the bath temperature of 80 °C, the formation of nanorod-like and nanotube-like structures is observed. The main effects of increasing the bath temperature are the improvement of the crystallinity of the deposits, the texturation of the films along the direction perpendicular to the substrate surface and the increase of the deposited quantities.

1. Introduction

In the last years, zinc oxide (ZnO) has attracted much attention owing to its various applications in the fields of optoelectronics, sensing, piezoelectric effect, magnetism or photovoltaic [1–3]. One important aspect of ZnO is the possibility to prepare a large range of nanostructures such as nanorods, nanotubes or nanorings [4,5]. Among the different available methods to obtain ZnO, electrodeposition has gained a great importance in the last decades, as it represents a low temperature (T < 100 °C) and cheap process. Moreover, the possibility to adjust the solution composition and the potential is a key point to generate structures ranging from dense films to nanostructures [6].

Boron Doped Diamond (BDD) electrodes present a number of exceptional properties, such as wide electrochemical windows, stability and resistance against corrosion, which are attractive for many applications. ZnO associated with diamond leads to heterojunctions with applications to photoluminescence [7], surface acoustic wave devices [8], or biosensors [9]. As ZnO/BDD heterojunctions are mainly prepared through solid routes like atomic layer deposition (ALD) or chemical vapor deposition (CVD) [7–9], in this work we have focused on the preparation of such heterojunctions through an electrochemical process.

In 2006, Chatterjee and Foord studied the electrochemical deposition (ECD) of ZnO on BDD [10] for the first time. Based on the reduction of nitrate (originated from $Zn(NO_3)_2$) as a precursor of hydroxides, they described the formation of a structure with a compact morphology, in which the diamond surface was covered with small ZnO grains of 500 nm.

In the present work, for the first time, the electrochemical deposition of ZnO structures on BDD substrates has been performed using the method based on the reduction of dissolved oxygen as a precursor pioneered by Peulon and Lincot [11,12]. Unlike $Zn(NO_3)_2$, using O_2 as a precursor of hydroxides allows the modulation, with the temperature, of $[OH^-]/[Zn^{2+}]$ ratio in the bath. In these conditions, the first step is the Oxygen Reduction Reaction (ORR) leading to the formation of OH^- according to Eqs. (1) or (2), followed by the precipitation of zinc hydroxide (3) and finally by its dehydration (4).

$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^- \tag{1}$$

$$O_2 + 2\,H_2O + 2\,e^- \rightarrow H_2O_2 + 2\,OH^- \tag{2}$$

$$Zn^{2+} + 2\,OH^- \rightarrow Zn(OH)_2 \tag{3}$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \tag{4}$$

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The influence of the bath temperature has been investigated from 20 °C to 80 °C. X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) were performed after the different ECD processes to determine the structure, the composition and the morphology of the resulting deposits.

2. Experimental

Electrochemical deposition has been carried out in a classical three-electrode cell with a volume of 300 mL, where a Zn wire has been used as the counter electrode and a Mercury Sulfate Electrode (MSE), placed in a separate compartment maintained at room temperature, has been used as reference. The working electrode is a polycrystalline BDD film with an area of 0.1 cm^2 and a thickness of 2.5–3 μm. The mean surface roughness, estimated through Atomic Force Microscopy (AFM) by the manufacturer, is of about 57 nm. The BDD films, provided by Neocoat, are grown on boron doped monocrystalline silicon in a hot-filament-assisted chemical vapor deposition reactor supplied with diborane and methane in hydrogen. The doping level, checked by Secondary Ion Mass Spectrometry (SIMS), is $N_A \approx 6 \times 10^{20}\ B \cdot cm^{-3}$. The diamond substrates are cleaned during 15 min in dichloromethane, then during 15 min in acetone, and finally rinsed with deionized water.

The ZnO structures are deposited in an aqueous solution made of 5 mM $ZnCl_2$ (Carlo Erba, purity >97%) and 0.1 M KCl (Alpha Aesar, purity >99%). To reach the saturation, molecular oxygen (O_2) was supplied to the solution by bubbling O_2 during 45 min prior to starting the experiment. A moderate bubbling of O_2 is maintained in the cell during the deposition process.

The ZnO depositions have been realized at a constant applied potential equal to − 1.4 V/MSE, during 1 h. Four bath temperatures have been investigated: 20 °C, 40 °C, 60 °C and 80 °C.

All the electrochemical measurements have been performed with a Parstat-2263.

The deposited films have been observed with a Jeol JSM 7001-F Field Emission scanning electron microscope, using an accelerating voltage of 5 kV. XRD has been performed on a Siemens D-5000 diffractometer using CuKα radiation ($\lambda = 1.5418$ Å; step size 0.02° (2Θ); angular range 20°–65° (2θ)).

XPS has been performed on a Thermo Scientific ESCALAB 250 Xi X-ray photoelectron spectrometer. The X-ray source is the monochromatic Al Kα radiation (1486.6 eV) with a pass energy of 20 eV (resolution 0.2 eV). The emission of photoelectrons from the sample is analyzed at a take-off angle of 90° under UHV conditions. Charge compensation is applied during acquisition with a flood gun. After collection, the binding energies are calibrated on the C1s signal having a binding energy BE = 285 eV. The accuracy of the reported binding energies (BEs) can be estimated to be ± 0.1 eV. The XPS peak areas are determined after subtraction of a flat background. The atomic ratio has been calculated after normalization using the Scofield factors of the investigated elements. All spectra processing has been carried out using Thermo Scientific™ Avantage Data System software. The spectral decomposition has been performed by using Gaussian–Lorentzian (70%/30%) functions.

3. Results and discussion

Before starting the ECD, cyclic voltammetry (*C-V*) experiments are conducted to establish the potential conditions for ECD of ZnO on BDD surfaces. At T = 20 °C, 40 °C, 60 °C and 80 °C, *C-V* measurements in deaerated electrolyte solutions containing 5 mM of $ZnCl_2$ and 0.1 M of KCl are performed (Fig. 1-a). As expected, Fig. 1-a shows that the overvoltage of Zn^{2+} reduction into metallic zinc increases with decreasing the bath temperature. A similar trend has been observed on other substrates in the same conditions [13–15]. The *C-V* curves show the formation of metallic Zn for potentials more negative than − 1.42, − 1.48, − 1.57 and − 1.75 V/MSE for bath temperatures equal to 80 °C, 60 °C, 40 °C and 20 °C respectively. Current–voltage curves in electrolyte solution saturated with dissolved molecular O_2 and containing 0.1 M of KCl (Fig. 1-b) have also been realized. The four bath temperatures have been tested to determine the potential range for the ORR on BDD. As on other substrates [16–18], we observe that the ORR overvoltage decreases with the increase of the bath temperature. ORR overvoltages, ranging from − 1.1 V/MSE to − 1.5 V/MSE (depending on the bath temperature) and current densities ranging from 0.1 to 1 $mA \cdot cm^{-2}$ are similar to values usually obtained on BDD substrates [19–21].

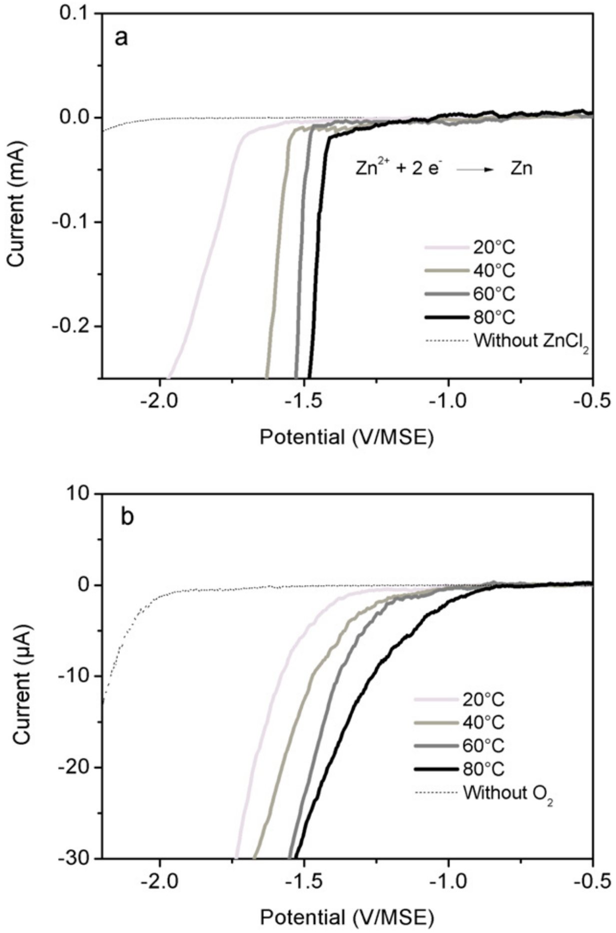

Fig. 1. a—Current–Voltage curves with BDD as working electrode in a deaerated solution made of 5 mM of $ZnCl_2$ and 0.1 M of KCl; the sweep rate is 50 $mV \cdot s^{-1}$. b—Current–Voltage curves with BDD as working electrode in a 0.1 M of KCl solution saturated with molecular oxygen; the sweep rate is 50 $mV \cdot s^{-1}$.

Hence, to both avoid the unwanted Zn formation and favor the ORR, all the electrochemical depositions have been carried out by setting the potential at − 1.4 V/MSE. It should be noted that this value is the usually applied potential for ECD of zinc oxide on many substrates [22–24].

3.1. Deposition: current–time (C–t) curves at 20 °C, 40 °C, 60 °C and 80 °C

Fig. 2 depicts the chronoamperograms corresponding to the deposition of ZnO on BDD films at − 1.4 V/MSE, during 1 h and for the four different bath temperatures. The recorded cathodic current, j_c, corresponds to the ORR (Eqs. (1) and/or (2)). Current transients can provide information on the ECD mechanism [12,22,25–27]. On BDD substrate, notable differences are observed for experiments made at 20 °C and at T ≥ 40 °C. For ECD performed at 20 °C, we observe a continuous decrease of $|j_c|$, from an initial value of about 50 $\mu A \cdot cm^{-2}$ down to almost zero. This behavior suggests that the BDD electrode becomes passivated by the deposition of a poorly conducting layer. Differently, for ECD performed at T ≥ 40 °C, $|j_c|$ values increase during the process and reach