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ScienceDirect
Journal of Electroanalytical Chemistry 598 (2006) 27–35
Journal of Electroanalytical Chemistry
www.elsevier.com/locate/jelechem

Statistical modelling of electrochemical deposition of nanostructured hybrid films with ZnO–Eosin Y as a case example

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Received 21 April 2006; received in revised form 10 July 2006; accepted 22 August 2006
Available online 11 October 2006

Abstract

We study models of electrodeposition of hybrid organic–inorganic films with a special focus on the growth of ZnO with Eosin Y. First we propose a rate equation model which assumes that the organic additives form branches with an exposed part above the ZnO deposit, growing with larger rate than the pure film and producing ZnO at the exposed length. This accounts for the generation of OH^- ions from reduction of dissolved oxygen near the branches and reactions with Zn^{2+} ions to form ZnO molecules. The film grows with the same rate of the branches, which qualitatively explains their catalytic effect, and we discuss the role of the additive concentration. Subsequently, we propose a statistical model which represents the diffusion of the hydroxide precursor and of eosin in solution and adopt simple probabilistic rules for the reactions, similarly to diffusion-limited aggregation models. The catalytic effect is represented by the preferential production of OH^- ions near eosin. The model is simulated with relative concentrations in solution near the experimental values. An improvement of the growth rate is possible only with a rather large apparent diffusion coefficient of eosin in solution compared to that of hydroxide precursors. When neighboring eosin clusters competitively grow, the increase in the growth rate and a high eosin loading are observed in the simulated deposits. Those features are in qualitative agreement with experimental results.

Keywords: Zinc oxide; Eosin Y; Cathodic electrodeposition; Growth model; Diffusion-limited aggregation

1. Introduction

The growth of thin films from solutions has emerged as an efficient, low temperature, versatile preparation route which can be used at large scale for the production of high quality materials [1]. One of the interests of these methods is the possibility of adding foreign soluble compounds to the deposition bath and modulating film properties by playing with the interactions which arise between the growing film and these compounds. Among the additives, organic ones are of utmost interest since many of them have been shown to act as templating agents and/or crystal growth directing agents, and in many cases as functionalizing agents for the deposits.

These effects are well-documented in the case of zinc oxide. This inorganic compound has attracted much attention due to a broad range of potential high technology applications such as surface acoustic wave filter [2], light emitting diodes [3], lasers [4], varistors [5], gas sensors [6] and solar cells [7]. ZnO can be prepared as a thin film by chemical deposition methods [8,9] or by electrodeposition [10–15]. The dramatic effects of organic additives on film structures and morphologies have been reported with both

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doi:10.1016/j.jelechem.2006.08.008

deposition routes. For instance, in the presence of citrate, chemically deposited ZnO are formed of stacked nanoplates assembled in a biomimetic manner [9]. However the most impressive morphological changes have been observed in electrodeposited zinc oxide. In the presence of sodium dodecylsulfate (SDS), the formation of lamellar nanostructures has been shown [16,17]. The SDS can be removed from the film and highly porous thin films are released [17]. Different dyes, such as Eosin Y (EY) [18–21], fluorescein (FL) [22], Tetrasulfonated phthalocyanines (TSPc) [23–26] and riboflavin (RI) [27], have also been shown to incorporate in the film and to give rise to nanostructures. These organic dyes contain negatively charged functions (carboxylate (EY, FL), sulfonate (TSPc) or phosphonate (RI) groups) which allow their direct binding to the oxide crystal surface during the synthesis.

While the effects of additives in film shaping are widely illustrated in experimental works, particularly that of the organic ones, the exact role of these compounds in the growth process remains to be clarified in most cases. The aim of the present work is to fill this gap by proposing kinetic and statistical models for zinc oxide electrodeposition in the presence of EY in solution, which focus on a small number of basic features of those processes. The starting point for this modeling is a series of experimental results, some of them also observed in deposition with different organic additives [17].

The first step of electrochemical zinc oxide synthesis is the cathodic reduction of a hydroxide precursor such as molecular oxygen [11,13], hydrogen peroxide [14,15] or nitrate ions [10,18]

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad (1)$$

$$H_2O_2 + 2e^- \rightarrow 2OH^- \quad (2)$$

or

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (3)$$

At a temperature slightly above room temperature [28], well crystallized zinc oxide with the wurtzite hexagonal structure is precipitated at the electrode surface

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O \quad (4)$$

In many cases, it has also been shown that the organic component presents catalytic properties for the deposition process. This catalytic effect is connected to the improvement of O_2 reduction (Eq. (1)) with EY [20], TSPc [26], SDS [17], whereas EY has also been shown to catalyze the H_2O_2 reduction (Eq. (2)) [19]. Thus, one of the assumptions of our models is a distinguished rate of formation of ZnO near the species that represent aggregated eosin molecules.

The zinc oxide films prepared in the presence of EY show large round shaped single crystals of zinc oxide filled with self-assembled dye aggregates, as shown in Fig. 1 [21]. It is observed that the dye can be almost completely removed by a soft chemical treatment [29,30], revealing a network of mesopores which is connected to the surface and can be filled with a solution. This network, formed by aggregated dye molecules, acts as a template for the growth of ZnO. In our models, these experimental facts justify the assumption of formation of connected branches of the species that represent the additive molecules in the films.

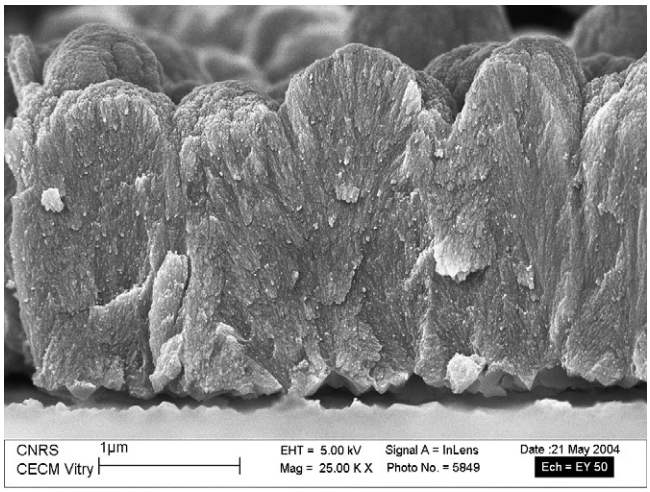

Fig. 1. FESEM cross-sectional view of a ZnO/EY thin film prepared by electrodeposition.

In Section 2 of this paper, we will introduce our first model, which is based on rate equations, and explains some features of the cooperative growth of a ZnO film and additive aggregates. This model is particularly useful for understanding the role of additive concentrations and diffusion coefficients in a qualitative way. Subsequently, in Section 3 we will present a statistical model which represents the main microscopic features of those processes by adopting probabilistic rules of diffusion and aggregation of some chemical species in solution and in the deposit. The hypothesis of a growth mechanism controlled by diffusion-limited aggregation of the eosin molecules was anticipated in Ref. [31]. Simulation results of that statistical model, presented in Section 4, provide estimates of growth rates, structures of ZnO and EY deposits and shows a role of diffusion coefficients which are in qualitative agreement with experimental findings. Finally, in Section 5 we summarize our results and present our conclusions.

2. Rate equation model

This model aims at explaining basic kinetic features of the growth of ZnO with organic additives with drastic simplifications of the film structure.

First we assume that pure ZnO growth takes place with rate r_0 (in nanometers per second), due to reactions of type (4) near the film surface. If the average volume occupied by one molecule is V, then r_0/V is the growth rate per unit area in that case. Even in the presence of the additives, the roughness of the ZnO film surface will be neglected.