

# The effects of deposition potential and H<sub>2</sub>O<sub>2</sub> concentration on electrochemically grown ZnO

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**Abstract** — This paper presents the results of electrochemical deposition of zinc oxide (ZnO) on zinc foil from zinc nitrate, zinc sulfate and hydrogen peroxide solutions. The equations of the chemical reactions taking place are presented. The morphology of the samples was found to be influenced by hydrogen peroxide concentration and the potential applied during growth. Also, the photoluminescence spectrum of the sample was influenced by the concentration of hydrogen peroxide. The dependencies mentioned are discussed and explained.

**Index Terms** — effect of deposition potential, effect of hydrogen peroxide concentration, electrochemical deposition, photoluminescence, zinc oxide.

## I. INTRODUCTION

Zinc oxide is a wide band gap semiconductor which has gained a lot of attention from the research community due to its unusual properties: 3.36 eV(r.t.) direct band gap, piezoelectricity, biocompatibility, gas sensitivity [1], etc. It has a high potential for applications in a wide area of fields: optoelectronics, photonics, biomedical and gas sensing applications.

The deposition of ZnO can be achieved using various ways: molecular beam epitaxy, metal-organic chemical vapor deposition, thermal transport and condensation, sol-gel, chemical bath, hydrothermal, electrochemical deposition, etc. Most of these are very expensive requiring high temperatures and/or vacuum systems, while chemical and electrochemical deposition offer simple technology, widely available materials and easy scalability.

The advantage of chemical deposition over the electro deposition is the fact that the substrate conductivity is absolutely of no importance and growth can be realized on any substrate whereas the electro deposition needs a conductive substrate. The advantage of electro deposition over the chemical deposition is the possibility to selectively grow structures on conductive regions of a substrate leaving the high resistivity regions uncoated, all this without the imperative need for a series of lithographic operations. Furthermore, if the electrodeposition technology develops to the state where it will allow controlling the characteristics of the nanostructures deposited using the electrical parameters, then the growth of nanostructures by electro-deposition will know a wide application due to the advantages of easily changing and adjusting electrical parameters over the solution composition.

While the growth mechanism [2] and the effects of time and temperature [3] have been investigated before, in this paper is presented the effects of deposition potential and hydrogen peroxide concentration.

## II. EXPERIMENTAL

The electrochemical deposition of ZnO was carried out using zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>) or zinc sulfate (ZnSO<sub>4</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solutions in a three-electrode cell configuration: the cathode was a 99.9 % SIGMA Aldrich Zn foil (working electrode), Ag/AgCl reference electrode and a Pt wire counter electrode. The temperature of the solution was maintained at 70°C by means of a magnetic stirrer with a heating table. The electrochemical deposition potential was stabilized with the help of a computer controlled GillAC potentiostat.

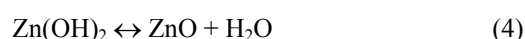
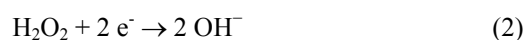
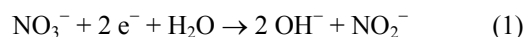
Prior to deposition the samples were rinsed in an acetone bath and dried in air at room temperature. After deposition, the samples were rinsed in distilled water and dried at room temperature.

The morphology and chemical composition microanalysis of samples were studied using a VEGA TESCAN TS 5130MM scanning electron microscope (SEM) equipped with an Oxford Instruments INCA energy dispersive X-ray (EDX) system.

The continuous wave (cw) PL was excited by the 351.1 nm line of an Ar<sup>+</sup> SpectraPhysics laser and analyzed with a double spectrometer ensuring a spectral resolution better than 0.5 meV. The samples were mounted on the cold station of a LTS-22-C-330 optical cryogenic system.

## III. RESULTS AND DISCUSSIONS

Upon the application of potential, the following reactions take place at the cathode:



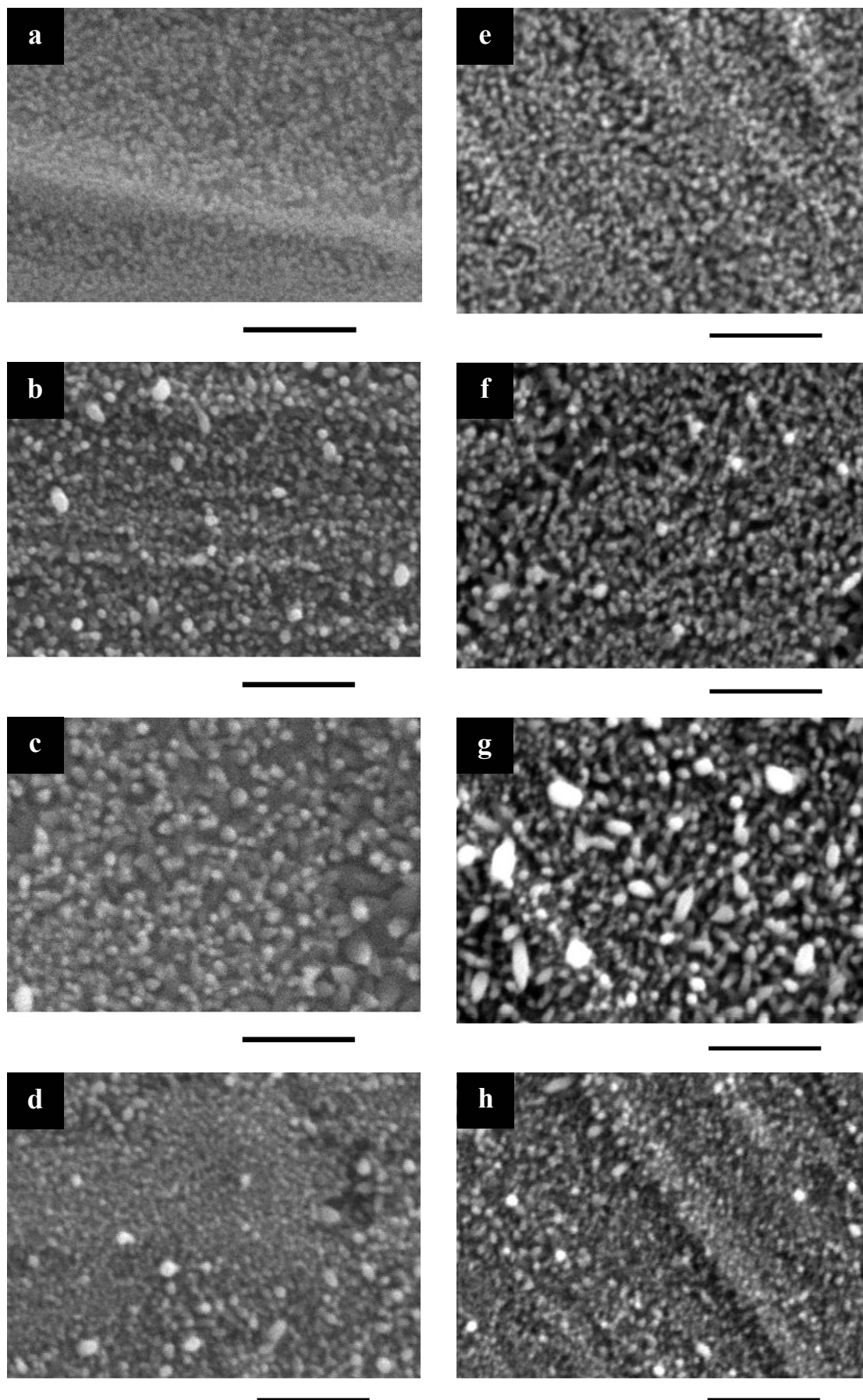


Fig. 1. SEM images of ZnO layers grown in 0.2mM Zn(NO<sub>3</sub>)<sub>2</sub> (a-d) and in 0.2mM ZnSO<sub>4</sub> (e-h) containing also H<sub>2</sub>O<sub>2</sub>: (a,e) 0, (b,f) 0.2 mM, (c,g) 0.4 mM and (d,h) 0.6 mM. The potential applied was 1.4 V/(Ag/AgCl) for a period of 1000 s. The scale bar is 2 μm.

Hydroxyl radicals are generated electrochemically, after which zinc hydroxide is formed and at temperatures above 60°C [4], the latter decomposes to water and zinc oxide, which in its turn deposits onto the sample.

To investigate the influence the zinc salt and of hydrogen peroxide concentration on the growth of zinc oxide layers, electrochemical deposition has been carried out for 1000 s employing 0.2mM  $Zn(NO_3)_2$  and 0.2mM  $ZnSO_4$  solutions with different peroxide concentrations: 0 (no peroxide), 0.2, 0.4 and 0.6 mM. The results of the SEM analysis of the morphologies obtained are presented in Figure 1 (a-d for  $Zn(NO_3)_2$  and e-h for  $ZnSO_4$ ). As one can see the dimensions of the structures grown increase with the concentration of hydrogen peroxide for low concentrations of the latter, and decrease when the concentration rises from 0.4 to 0.6 mM. The increase in dimensions can be explained by the increase in the hydroxyl radical generation rate and consequently in a higher deposition rate from the solution resulting in larger structures. The following decrease observed at higher concentrations can be accounted for by the fact that when the ZnO generation rate is higher than the rate of crystallization, the species in the solution don't make it to the appropriate position in the crystal lattice because they attach to one another since they are too close as compared to the distance to the crystal, and as a result they conglomerate and the deposition morphology presents granular structures. The different anions of the zinc salts don't show any significant influence, the dimensions and morphologies being similar.

The influence of the potential applied on the morphology of the structures growing on the substrate was studied by applying different potentials to the working electrode: 1.3 V/(Ag/AgCl), 1.5 V/(Ag/AgCl), 1.7 V/(Ag/AgCl) in a solution containing 0.2mM  $Zn(NO_3)_2$  and 0.2mM  $H_2O_2$  for 1000 s. The morphologies produced can be seen in the

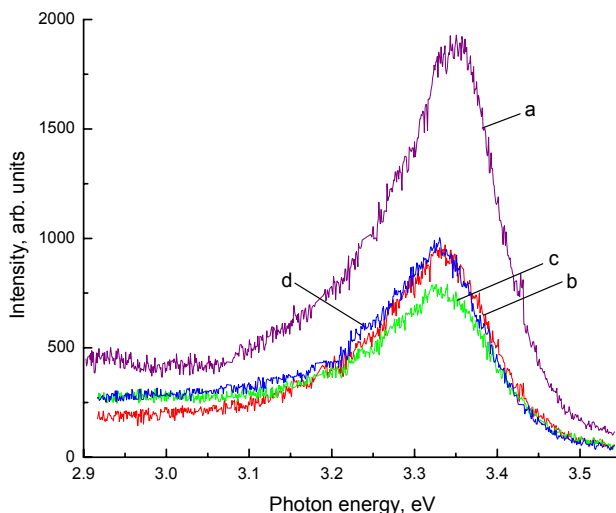


Fig. 2. Photoluminescence spectra measured from the samples produced by electrodeposition in a 0.2mM  $(Zn(NO_3)_2 + x H_2O_2)$  solution during 1000 s at a 1.4 V/(Ag/AgCl) potential, where x is: a) 0, b) 0.2 mM, c) 0.4 mM and d) 0.6 mM.

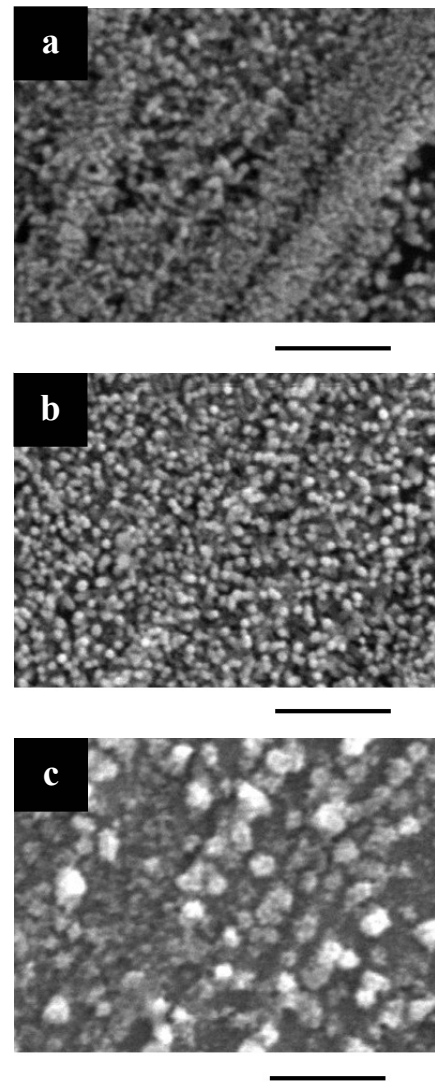


Fig. 3. SEM images of ZnO structures deposited at different potentials: a) 1.3 V/(ref.), b) 1.5 V/(ref.), c) 1.7 V/(ref.) in an equimolar 0.2mM  $(Zn(NO_3)_2 + H_2O_2)$  solution during 1000 s.

SEM images shown in Figure 3. The changes in the structure morphology can be described as increasing size from (a) to (b) and decreasing size from (b) to (c) and transition from nanorod array to granular-dendritic structure.

The reason for this dependence is analogous to that for the morphology dependence on the hydrogen peroxide concentration: the deposition rate is increasing due to the increasing supersaturation level, which leads to a higher deposition rate, and consequently, to larger structures and, finally, to the transformation of nanorods into dendritic conglomerates of granules.

The results of the optical characterization are presented in Figure 2. The photoluminescence spectra were taken from the samples the SEM images of which are presented in Fig. 1. (a-d). The spectra show a wide PL band corresponding to the ZnO near-bandgap transitions. The peak intensity of the near-bandgap luminescence is decreasing with the increase of the hydrogen peroxide concentration, indicating a decreasing quality of the material. This is consistent with the fact that the increasing

supersaturation level of the species in the solution, taking place at low hydroxyl concentration (close to neutral pH) leads to the increase in the formation rate of the ZnO structures and low defect re-dissolution rate, and consequently, to distancing from the quasi-equilibrium conditions [4].

#### IV. CONCLUSION

In this paper, the electrochemical deposition of ZnO was demonstrated. Also, the dependency of the morphology and photoluminescence spectrum on the hydrogen peroxide precursor concentration and the dependency of the morphology on the potential applied during growth have been presented and explained according to general principles of chemistry and crystal growth as understood by the author.

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