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Structural and optical properties of ZnO nanocrystals growth by the chemical bath deposition

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ABSTRACT

ZnO films prepared on glass substrates at T = 80 °C ± 3 °C using the chemical bath deposition technical. The precursor solutions was KOH (0.5 M), NH_4NO_3 (1.5 M) using three different $Zn(NO_3)_2$ (0.2 M, 0.3 M, 0.4 M) concentration. The morphology is investigated by Scanning Electron Microscopy (SEM) and images shows porous matrix with cavities of different size, javelin and tretrap. According to the XRD diffractograms, all the nanocrystals present hexagonal crystalline phase with grain size of ∼33.4 nm, ∼36.5 nm and ∼34.2 nm. The samples present typical stress in these films. Absorbance spectrum exhibits a characteristic band of the nanocrystals, band gap energy shows a shift in the range ∼3.7–3.8 eV associated with decreasing grain size, as well as the quantum confinement effect in this case of nanocrystalline material. Photoluminescence shows bands, associated with the existence of interstices and vacancies of oxygen and Zinc respectively. Analysis of chemical reactions is performed using the Nernst equation to quantify changes ΔG° to predict the spontaneity of the reactions.

1. Introduction

Among various transition metal oxides, zinc oxide (ZnO) has attracted interest in many areas of chemistry, physics and material science, as a wide band gap energy (E_g ∼3.37 eV) [1], this property makes it of importance for a great variety of applications including blue/ultraviolet (UV) optoelectronic devices and piezoelectric devices. In addition to own large ZnO exciton binding energy (∼60 mV) makes this oxide an candidate strong for room-temperature lasing, and presents the possibility of further improving lasing conditions due to quantum confinement effects, which is of interest in the last decade [2]. The associated parameters for the control of the morphology in the growth of ZnO nanocrystal have been objective of studies, these control has increased attention due to the fact they play very important rules in determining optical, electrical, magnetic properties [3]. ZnO presents different and extraordinary morphologies, such as nanocombs, nanorings, nanohelixes, nanosprings, nanobows, nanobelts, nanowires, tetrapds and javelin and have been synthesized under specific growth conditions. Many synthesis methods have been used to prepare ZnO; magnetron sputtering [4], sol-gel [5], solid-vapor [6], etc. We review the current status of research into ZnO javelin and tetrapod nanocrystals as well as the changes in the structural and optical properties associated with the different morphologies. The photoluminescence of ZnO films typically

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consists of a near-band-edge emission and a deep level emission [7] and in this work the photoluminescence associated with the morphological changes in these thin films is investigated. The control of crystal growth at interfaces is fundamental to a wide range of processes of scientific interest, and this fact attracts a particular interest. Such behavior has received considerable attention for the fabrication of thin film semiconductors, where the properties can be tuned according to the degree of strain introduced into the supported thin film. In the present work we present some preliminary experimental results in ZnO films synthesized by chemical bath deposition (CBD). The mentioned films are grown using three different molar concentrations (MC) keeping the other constant standard parameters (agitation, temperature, pH, etc.).

2. Experimental details and chemical reactions

The chemical reactions of ZnO by CBD, are investigated using numerical values of the standard potential of semi-cell (ε°) [8]. The free energy change of Gibbs (ΔG°) is evaluated through the relationship; $\Delta G^\circ = -n\tau\varepsilon^\circ$, where: ε° (V) is the half-cell potential, τ the Faraday constant ($\tau \sim 96500$ coul/equivalent), n the number of equivalents or electrons transferred from one element to another. The different stages of the chemical equilibria are shown below:

In this report, we propose as intermediary the ZnO_2^{2-} ion which has been reported before [9]. The indirect formation of ZnO_2^{2-} complex ion, which is generated according to the following equilibrium

$$Zn^{2+} + 4OH^- \Leftrightarrow ZnO_2^{2-} + 2H_2O \quad \Delta G^\circ = -8.27 \text{ kJ} \tag{1}$$

On the other hand, the intermediate complex of coordination $[Zn(NH_3)_4]^{2+}$ ion tetramínzinc, releases slowly Zn^{2+} ion, as it has been proposed in the case of Cd^{2+} in the typical reaction for the synthesis of the CdS, presenting the following equilibrium:

$$[Zn(NH_3)_4]^{2+} \Leftrightarrow Zn^{2+} + 4NH_3 \quad \Delta G^\circ = +53.30 \text{ kJ} \tag{2}$$

From Eq. (2) it is observed that $\Delta G^\circ > 0$, therefore is non-spontaneous and the slow release of the Zn^{2+} ion is favored, this is a key parameter to control the spontaneous precipitation of ZnO. As mentioned above, in our working conditions the following chemical equilibria are proposed:

$$[Zn(NH_3)_4]^{2+} + 4OH^- \Leftrightarrow ZnO_2^{2-} + 2H_2O + 4NH_3 \quad \Delta G^\circ = -28.97 \text{ kJ} \tag{3}$$

The k_{eq} for the complex ion (2) is given by [10]

$$k_{eq} = \frac{[Zn(NH_3)_4]^{2+}}{\left[Zn^{2+}\right][NH_3]^4} = 10^9 \tag{4}$$

ZnO has been obtained [11]

$$Zn^{2+} + CO(NH_2)_2 \Leftrightarrow ZnO + 4NH_3 + CO_2 \uparrow \tag{5}$$

On the other hand, Yushida. et al. reported the following equilibria [12]

$$Zn^{2+} + NO_3^- + 2e^- \Leftrightarrow ZnO + NO_2^- \quad \Delta G^\circ = +47.47 \text{ kJ} \tag{6}$$

$$5Zn^{2+} + NO_3^- + 2H_2O \Leftrightarrow 5ZnO + NH_4^+ + 8e^- \quad \Delta G^\circ = +41.10 \text{ kJ} \tag{7}$$

According to Eqs. (6) and (7), $\Delta G^\circ > 0$ are non-spontaneous reactions. In our opinion, this model, which considers the indirect formation of $[Zn(NH_3)_4]^{2+}$ and ZnO_2^{2-} ions respectively is performed according to

$$[Zn(NH_3)_4]^{2+} + ZnO_2^{2-} \Leftrightarrow 2ZnO + 4NH_3 + 2e^- 5 \quad \Delta G^\circ = +7.13 \text{ kJ} \tag{8}$$

In our work, NO_3^- and NH_4^+ ions, are generated by dissociation of $ZnNO_3$ and NH_4NO_3 in alkaline medium (pH ~8.3), these favors the formation of ZnO as well as with ΔG° decrease [12]. Significant numerical differences in ΔG° when compared with our theoretical calculations, these can be associated considering that Zn^{2+} ion in basic medium behaves as weak acid and in acid medium is weak base and these behavior is well known as an amphoteric. ZnO_2^{2-} ion in solution as an intermediate species. According to our experimental results, we consider what is mentioned before; ZnO_2^{2-} and OH^- ions act as catalysts favoring the formation of ZnO. Dissociation of $Zn(NO_3)_2$ in alkaline medium, generates Zn^{+2} ions; under these conditions the KOH provides the alkaline medium releasing OH^- and captured by $[Zn(NH_3)_4]^{2+}$ ion, this interacts with the ZnO_2^{2-} and OH^- ions thus generating the complex $[Zn(NH_3)_4]^{2+}ZnO_2^{2-}$, then the slow decomposition of $[Zn(NH_3)_4]^{2+}(OH^-)_2$. Initially by electrostatic attraction is adsorbed around the ZnO core, this decreases its surface energy by creating active sites on its surface. The changes in ΔG° obtained by us, are numerically close to those reported [12] and in both cases the reactions are non-spontaneous.