Electrochemically-induced coprecipitation of thin films in the zinc oxide / europium oxide system

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Wet methods like chemical bath deposition or Electrodeposition emerged for the preparation of high quality oxide thin films. The electrodeposition of ZnO can be considered as an electrochemically induced chemical bath deposition process.

The general mechanism consists in an electroreduction of an oxide precursor such as $O_2^{[1,\ 2]}$ or $H_2O_2^{3}$ into hydroxide ions. This leads to a pH increase in the vicinity of the electrode and to a local supersaturation for oxide precipitation which conducts to the formation of oxide thin film on the electrode surface. With O_2 , the mechanism can be summarized as :

$$1/2 O_2 + 2 e^{-} + H_2O \rightarrow 2 HO^{-}$$

 $M^{n+} + n HO^{-} \rightarrow MO_{n} + n/2 H_2O$

Zinc oxide is a transparent n-type semiconductor with a large bandgap 3,3 eV. ZnO thin films present interesting properties which are used for different applications such as piezoelectric transducers, chemical sensors, catalytic material, active layer in photovoltaic solar cells or laser diodes. Incorporation of a rare earth element such as europium⁴ (III) can bring property of luminescence to the ZnO film.

In this way, have extended we electrochemically induced coprecipitation with zinc oxide and europium oxide as a case example. The advantage of the method is the possibility of introducing foreign elements in the deposition bath to change the optical properties of the films, as we have already done with a xanthene dye, eosin Y³. First, an analysis of the solubility of ZnO and Eu(OH)3 has been realised in the KCl medium (Figure 1). Then we have studied the effect of the addition of europium (III) ions at different concentrations to the electrolysis bath. The films have been characterized by scanning electronic microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS). The insertion of europium has been proved by EDXS (Eu/(Zn+Eu) ranging from 6 to 80 at.%). In respect to the increasing concentration of Eu³⁺ in solution, an interesting morphological transition has been evidenced with the gradual vanishing of the hexagonal crystallites. We have also studied the effect of thermal treatment on the films. Supplementary experiments are now in progress in order to decrease the europium concentration down to 1% in ZnO and to control its oxidation state at +III. We will analyse the correlation between the properties of the films and the conditions of synthesis.

Références :

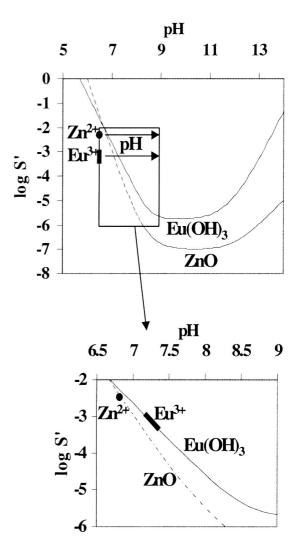


Fig. 1: Solubility of ZnO and Eu(OH)₃ in KCl 0.1 mol.L⁻¹ (zoom corresponds to the working zone)

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