OXIDE SYNTHESIS BY MAGNETOELECTRODEPOSITON

DALTIN A.L., BENAISSA M., CHOPART J.P. LISM, EA4695, URCA, B.P. 1039 - 51687 Reims Cedex 2 - France. al.daltin@univ-reims.fr

Abstract : Electrodeposition under superimposition of uniform magnetic field is appearing as a new method for the synthesis of oxides and doped-oxides. In this study, copper-doped ZnO and manganese-doped Cu_2O deposits were prepared and magneto-induced effects on electrocrystallization have been investigated. Comparison was made with electrodeposition obtained without magnetic field. The electrochemical behaviour, the morphology, the chemical composition and the structure of the deposits were discussed. Modifying oxide growth and final morphology with magnetohydrodynamic effects were observed.

1. Introduction

Magnetoelectrodeposition, i.e., electrodeposition under the superimposition of a magnetic field on the electrochemical cell, is largely used in the case of metal or alloy thin films synthesis, but up to now, very few papers concerned oxide deposits [1-6]. The effects of magnetic field on electrodeposition have been underlined by several authors [7-9] and could generate very promising potential applications [10]. These effects include modifications of electrocrystallization kinetics [3], growth process [5], morphology [6], texture, composition and smoothness of the deposit [10 and references therein]. These modifications, due to magnetically induced convective effect called magnetohydrodynamic (MHD) effect, take place at the cathode-electrolyte interface and could modify electrochemical reactions. Also microscopic minute vortexes, called micro-MHD flow could undergo [11]. Depending on the orientation of the cathode relative to the magnetic field orientation and the species in presence, some forces can be created such as the Lorentz force (F_L), the magnetic gradient force (F_B) and the paramagnetic force (F_P) (this later force, if paramagnetic species are under mass transport control).

Cathodic electrolytic deposition has been used in the past until today for the synthesis of numerous oxides reviewed in different papers [12-15]. The interest of the electrochemical synthesis of oxides in a one-step process at low temperature lies in fast and low-cost production.

In this paper Mn-doped Cu₂O has been studied for the promising defect-induced ferromagnetism. Up to now, the origin of the high T_c ferromagnetism in Cu₂O base dilute semiconductors (DMSs) is not well understood. Defects and therefore synthesis modes are responsible for these magnetic properties. It has been shown that both the positions of the doping transition-metals (substitutional or interstitial Mn atoms) and the vacancies have strong influences on the ferromagnetism of the doped Cu₂O [16-17]. Previous results on *Cu₂*. $_xMn_xO$ electrodeposition have been reported [18], indicating that the ferromagnetic properties can be tuned simply by controlling electrochemical growth conditions. On the other hand, it has been shown that magnetic field brings modification on the electrocrystallization of Cu₂O [5-6]. Here the electrodeposition of copper oxide (with or without Mn doping) is reported with various Mn concentrations under 1T magnetic field superimposition. This paper reports also on the growth of Cu-doped ZnO nanostructures by magnetoelectrolysis. ZnO has been extensively studied because of its large band gap (3.2 eV) with large exciton binding energy (60 meV) at room temperature and its wide applicability in functional devices [19-21].

Among doped ZnO materials, some of them can provide dilute magnetic properties such as room temperature ferromagnetism observed in Cu- doped ZnO [22].

2. Experimental section

Here oxides and doped-oxide were electrodeposited on an indium tin oxide (ITO) covered glass using a three electrode set-up. The working electrodes (WE) of about 1 x 2 cm were cleaned before deposition by immersion in an ethanol solution, followed by drying in air. The counter electrode was a Pt wound wire and the reference electrode, the Ag/AgCl one. A glass double-wall cell was used to maintain a constant temperature for all experiments. This cell was put inside the gap of a Drusch EAM 20G electromagnet. A constant and homogeneous magnetic field with amplitude up to 1T, oriented parallel to the horizontal upward electrode surface was applied during experiments with superimposed magnetic field. The electrolytes of this study were prepared from deionised water and analytical grade chemicals. The cathodic depositions of the ZnO and copper-doped ZnO were performed at 80°C from chloride electrolytes with the compositions and conditions listed in table 1. The cathodic depositions of the Cu₂0 and maganese-doped Cu₂0 were performed at 60°C from sulfate electrolytes with the compositions listed in table 2. The depositions were carried out in a potentiostatic mode with a potentiostat-galvanostat PGZ 300 Radiometer Analytical.

	[ZnCl ₂]	[KCl]	[CuCl ₂]	Т	pН	- E	t	В
	Μ	Μ	Μ	°C	-	V/AgAgCl	S	Т
ZnO	5.10^{-3}	0.1	0	80±2	5.7±0.3	1.05	9000	0-1
Cu-doped ZnO - A	5.10^{-3}	0.1	3.10-6	80±2	5.7±0.3	1.05	9000	0-1
Cu-doped ZnO - B	5.10-3	0.1	6.10-6	80±2	5.7±0.3	1.05	9000	0-1

Table 1 Electrolytes compositions and conditions of ZnO and Cu-doped ZnO depositions

	[CuSO ₄]	$[C_3H_6O_3]$	[MnSO ₄]	Т	pН	-E	-Q	В
	М	Μ	М	°C		$mV_{/AgAgCl} \\$	С	Т
Cu ₂ 0	0.4	3	0	60±2	10±0.3	200	1	0-1
Mn-doped Cu ₂ O - A	0.4	3	10 ⁻³	60±2	10±0.3	200	1	0-1
Mn-doped Cu ₂ O - B	0.4	3	10 ⁻²	60±2	10±0.3	200	1	0-1

Table 2 Electrolytes compositions and conditions of Cu₂0 and Mn-doped Cu₂O depositions

The deposits were examined by employing a scanning electron microscope (SEM) JEOL JSM 6460LA and chemical compositions were determined by an EDS JEL 1300 Microprobe coupled with the SEM. The crystalline structure was determined by X-ray diffraction (XRD) using a BRUKER D8 ADVANCE X-ray diffractometer coupled with a copper anticathode ($\lambda_{CuK\alpha} = 1.5056$ Å).

3. Results and discussion

Figure 1 A shows the variation of the current as a function of the deposition time recorded during the deposition of the deposits conducted with conditions of table 1. The steady-state

current decreases with magnetic field superimposition. Under B = 1 T, the steady state current increases with CuCl₂ concentration. XRD diffractograms of ZnO and doped-ZnO in figure 1B confirm the ZnO zincite structures (ICDD 36-1451) of the deposits obtained under 1T magnetic field as for deposits electrodeposited without magnetic field superimposition. This phase belongs to hexagonal crystal system. The diffraction peaks intensities of ZnO (100) decrease with CuCl₂ concentration. The highest intensities are for planes (100) and (101) as it has already shown for ZnO flower-like structures [23]. Figures 2 present some SEM top views of the different deposits obtained with or without a 1 Tesla magnetic field amplitude superimposition for respectively 0, 3 μ M and 6 μ M of doping concentration of copper chloride in the solution at different magnifications. These micrographs show that when magnetic field is superimposed on the electrochemical cell during ZnO electrodeposition, the nanostructures arrange themselves into homocentric bundles, which is not the case without magnetic field superimposition. When copper is introduced in the electrolyte solution, the growth mechanism changes.



Figure 1: A: Current time (I-t) curve of ZnO deposits from electrolytes with 0 (a,d), $3\mu M$ (b,e) and $6\mu M$ [CuCl₂] (c,f) under 0T (a-c) or 1T (d-f). B. XRD diffractogram of ZnO deposits from electrolytes with (a) 0,(b) 3 and (c) $6\mu M$ [CuCl₂] under 1T.



Figure 2: SEM images of Cu-doped ZnO nanostructures obtained by electrodeposition at a potential E = -1.05V/AgAgCl with different CuCl₂ electrolyte concentrations: (a,d) 0 μ M, (b,e) 3 μ M, (c,f) 6 μ M, under magnetic field superimposition: (a-c) B = 0 T and (d-f) B = 1 T at a magnification of X 5000.



Figure 3: Current time (I-t) curve of Cu₂O deposits from electrolytes with 0 (a), 10^{-3} M (b) and 10^{-2} M [MnSO₄] (c) under 0T or 1T.



Figure 4. XRD diffractogram of Mn-doped Cu_2O deposits from electrolytes with 10^{-2} M [MnSO₄] for 0 and 1T magnetic field superimposition.



Figure 5: SEM images of Mn-doped Cu₂O electrodeposited at a potential E = -1.05V/AgAgCl with different MnSO₄ electrolyte concentrations: (a,d) 0 M, (b,e) 10^{-3} M, (c,f) 10^{-2} M, under magnetic field superimposition: (a-c) B = 0 T and (d-f) B = 1 T at a magnification of X 5000.

The mechanism for the electroprecipitation of the ZnO nanorods is given in the following equations

$$O_2 + 2 H_2 O + 4e^- \to 4 O H^-$$
(1)
$$Z_2^{2+} + 2 O H^- \to Z_2 O + H O$$
(2)

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

Also the shape of ZnO deposited in baths of chloride could be hexagonal pillar or obelisk, due to the adsorption of Cl⁻ on the {0110} planes more easily than on (0001) plane [24]. The MHD convection promotes the growth of larger nanorods due to a higher concentration of Zn^{2+} near the external surface, and a higher aspect ratio due to the higher chloride concentration. Moreover, the shape of ZnO particles changes from needle to hexagonal obelisk nanorods with magnetic field superimposition. Homocentric bundles corresponding to

multipod structures obtained under magnetic field result from initial nucleation followed by the growth of the obelisk shaped ZnO around these nuclei. The μ MHD convection could be responsible for the growth of branches on the initial nuclei giving homocentric bundles. For deposits with high copper chloride concentration, these branches at the base of the central pillar are finer than the latter. Figure 3 shows chronoamperometric curves of Cu₂O (a) and Mn-doped Cu₂O (b-c). Also here the current intensities decrease with magnetic field superimposition for the three electrolyte compositions. As these deposits were obtained in the coulometric mode, the time is increased when the electrodeposition is made under magnetic field. XRD patterns (Figure 4) of the deposits indicate that the cuprite (ICDD 05-667) is the only phase present in all cases. (110) and (111) are more intense under magnetic field than without. Here, octahedral crystals, bigger under B = 1T, were synthesized and do not completely covered the ITO substrates (Figure 5). With Mn incorporation, smaller crystallites with higher Mn concentration under magnetic field appear.

4.Conclusion

The various studies presented in this paper illustrate the challenge of tuning morphology or composition by applying magnetic field on electrodeposition of oxide and doped-oxide. Both magnetohydrodynamic convection and micro-MHD effect induce modifications from the beginning of the growth process.

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4. References

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