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ELECTRODEPOSITION AND ANODIZING OF ZnMn ALLOY SUBMICRON WIRES

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The study of the electrodeposition and anodic oxidation processes of ZnMn alloy submicron wires is reported; ZnMn wire arrays were electrodeposited using a pulse current technique and an aqueous solution containing 0.2 mol dm^{-3} Zn(II)-EDTA + 0.2 mol dm^{-3} $MnSO_4$ + 0.6 mol dm^{-3} sodium citrate. The obtained alloy was anodized at a current constant density, in a methoxyethanol solution containing sodium hydroxide and in an aqueous potassium zincate solution. Photoluminescence spectra and SEM images showed the presence of the oxide layer on the surface of the anodized ZnMn wires.

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1. Introduction

Zinc oxide is a semiconductor with a wide band gap and natural n-type electrical conductivity, having a wurtzite structure. By replacing a fraction of cations of this host semiconductor material with transition metal ions could be obtained a promising diluted magnetic semiconductor (DMS) material for spintronics applications [1-4]. It was predicted that some of these materials should be ferromagnetic above room temperature [1-4]. By doping ZnO structures with transition metals ions, such as manganese or cobalt ions, may lead to the formation of various precipitates, which could have an influence on the magnetic properties [5,6]. Mn is known to be a fast diffuser in ZnO, which results often in highly inhomogeneous doping, formation of foreign phases as well as Mn precipitates. Low temperature growth conditions should be selected to minimize Mn diffusion and formation of various Mn-related oxide.

The aim of this work was to investigate the processes of the electrodeposition and anodic oxidation of ZnMn alloy wires prepared by template method, in order to obtain manganese doped ZnO wires.

2. Experimental

The synthesis of metallic wires was performed using a 30 μm thick polycarbonate membrane (Makrofol N, Bayer) with pore diameter around 600 nm and pores density 10^8 cm^{-2}. A thin gold film, which was to play later the role of the cathode for the codeposition of Zn and Mn, was deposited by sputtering on one side of the membrane; this film was subsequently reinforced by electrochemical deposition of copper. The chemical compositions of the solutions used to investigate the preparation process of ZnMn alloy microwires and their anodizing are presented in Table 1. ZnMn alloy wires were electrodeposited using a pulse technique [7] from the solution 1. Supplementary, in a comparative voltammetric study, similar solutions but without manganese compound (solution 2) and without zinc compound (solution 3) were used. The electrodeposition of ZnMn alloy was carried out at room temperature in a glass cell with a platinum foil (surface

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area 4cm^2) as counter electrode and a commercial saturated calomel electrode (SCE) as the reference electrode. The surface area of the membrane exposed at electrodeposition solutions (1-3) was 2cm^2. After the electrodeposition process the polymer membrane was dissolved in dichloromethane. The ZnMn wires were anodized to various voltages at 0.075 mAcm^{-2} current density either in organic solution 4 [8] or in aqueous solution 5. The electrochemical measurements were carried out with an Autolab PGSTAT 30 potentiostat/galvanostat connected to a computer. The metallic and oxide wires were imaged by scanning electron microscopy (SEM), using a FEI Quanta InspectF Scanning Electron Microscope equipped for chemical composition measurements with an EDX device from EDAX. X-ray diffraction (XRD) analyses were performed on a Bruker D8 Advance apparatus, using Cu-K$_\alpha$ radiation with λ=0.15405 nm. Photoluminescence (PL) spectra have been recorded using a lock-in technique and a standard luminescence set-up consisting in two monochromators for excitation and emission, a Xe-150W lamp as light source and a photomultiplier as light detector.

3. Results and discussion

Table 1. Chemical composition of the used solutions.

Solution	Composition
1	0.2 mol dm^{-3} Zn(II)-EDTA + 0.2 mol dm^{-3} $MnSO_4$ + 0.6 mol dm^{-3} sodium citrate aqueous solution, pH 5.8 [7]
2	0.2 mol dm^{-3} Zn(II)-EDTA + 0.6 mol dm^{-3} sodium citrate aqueous solution, pH 5.8
3	0.2 mol dm^{-3} $MnSO_4$ + 0.6 mol dm^{-3} sodium citrate + 0.2 mol dm^{-3} EDTA aqueous solution, pH 5.8
4	0.0125 mol dm^{-3} NaOH + 0.1 mol dm^{-3} hexamethylenetetramine in methoxyethanol
5	Potassium zincate saturated aqueous solution prepared as in [8]

Fig.1a presents comparatively linear voltammograms obtained for cathodic process in solutions 1-3 listed in Table 1 at a sweep rate of 5 mVs^{-1}, using polycarbonate membranes. The cathodic scan shows clearly an increase of the cathodic current in the potential region –1 ÷ -1.5 V and a peak at around -1.3 V for ZnMn or Zn deposition) to formation of metallic deposit [9], followed by a sharp increase of current assigned to massive hydrogen formation and evolution. The manganese reduction peak obtained in solution 3 is observed at around -1.1 V.

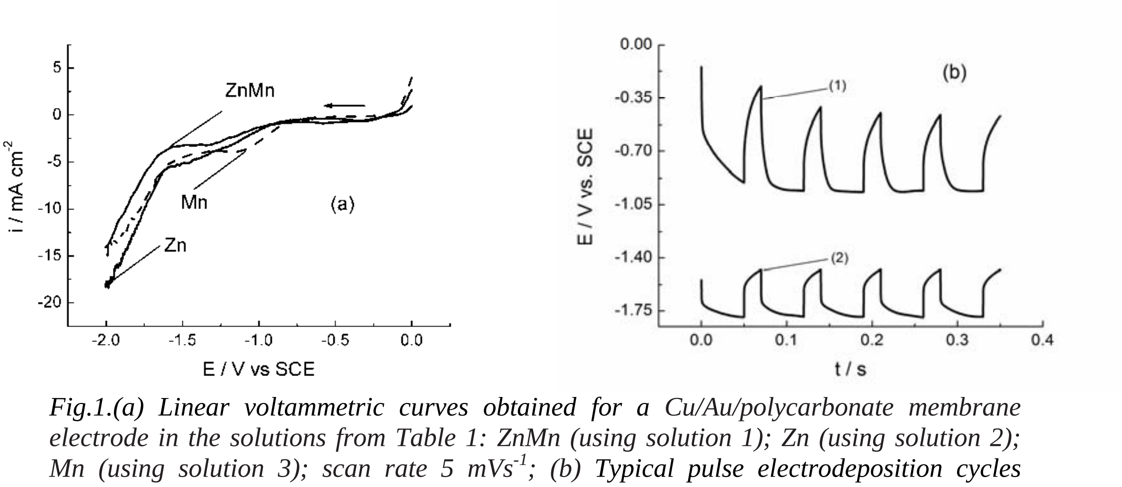

Fig.1.(a) Linear voltammetric curves obtained for a Cu/Au/polycarbonate membrane electrode in the solutions from Table 1: ZnMn (using solution 1); Zn (using solution 2); Mn (using solution 3); scan rate 5 mVs^{-1}; (b) Typical pulse electrodeposition cycles showing the voltage recorded during the cathodic and rest stages: 1) the first cycles; 2) after 30 min cycling

The results suggest that the electrodeposition of zinc in membrane pores takes place together with hydrogen evolution, although a model [10] for the electrodeposition of zinc in acidic sulphates electrolytes also proposed the formation of ZnH, ZnO, ZnOH species in the cathodic peak region.

Experimental investigations have shown that the pores are filled non-uniformly [11] using direct electrolysis current for the deposition. In our experiments, we prepared ZnMn alloys as wires by pulse plating during 70 min, with a cathodic pulse of current density of 7 mAcm^{-2} applied for 50 ms (pulse time), followed by a relaxation time of 20 ms corresponding to the current interruption. The resulted voltage cycles during filling of the membrane pores are presented in Fig.1b, where an important shift of deposition potential toward high cathodic potentials is observed; this phenomenon may be attributed mainly to the diffusion of metallic ions inside the membrane pores.

Fig. 2 shows SEM images of ZnMn wires grown vertically from Cu/Au substrate having around 600 nm in diameter; one can observe that the pulsed electrodeposition led to a stratified growth of the wires.

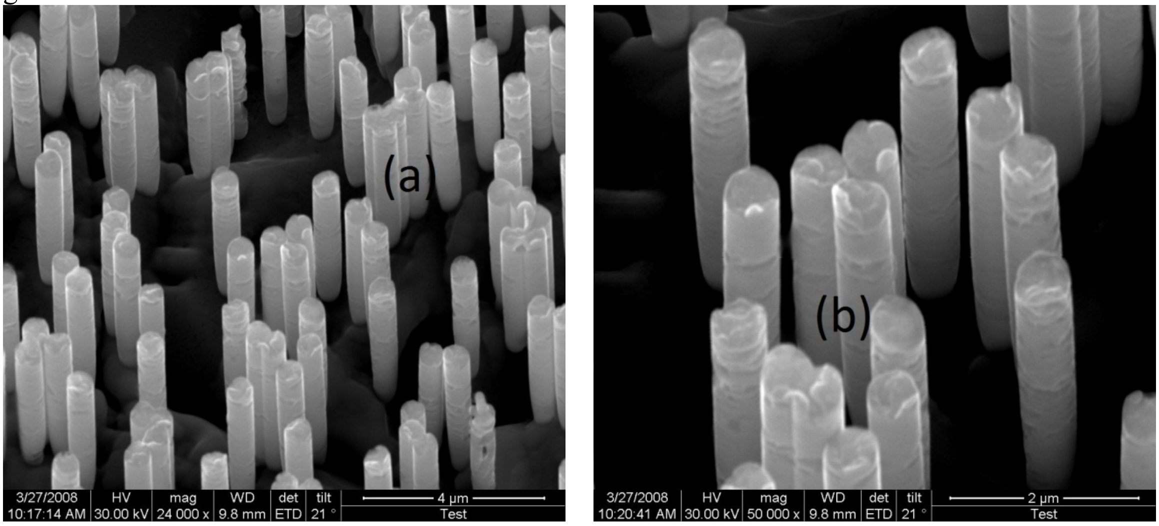

Fig.2. SEM micrographs of ZnMn wires grown into pores of polycarbonate membrane) by pulse electrodeposition, with a cathodic current density of 7 mAcm^{-2}; t_{pulse}=50 ms, t_{off}=20 ms; (a) general view; (b) detail

In order to discuss a possible mechanism for obtaining manganese doped ZnO wires by ZnMn alloy anodizing, we mention that the involved intermediate products must be insoluble in the solution used for anodization.

Thus, in solution 4 containing sodium hydroxide, the anodic process could be described by the following equations of EC mechanism:

$$Zn - 2\,e^- \rightarrow Zn^{2+} \qquad (1)$$

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

The anodizing process of zinc deposit in solution 5 can be simply represented by another EC mechanism, involving the equation (1) followed by a chemical precipitation according to eq. (3) [8]:

$$Zn^{2+} + Zn(OH)_4^{2-} \rightarrow 2\,ZnO\downarrow + 2\,H_2O \qquad (3)$$

Fig. 3a shows the dependence of anodic current density of the electrode potential during anodic polarization of ZnMn wire array electrode in the solutions 4 and 5, respectively.

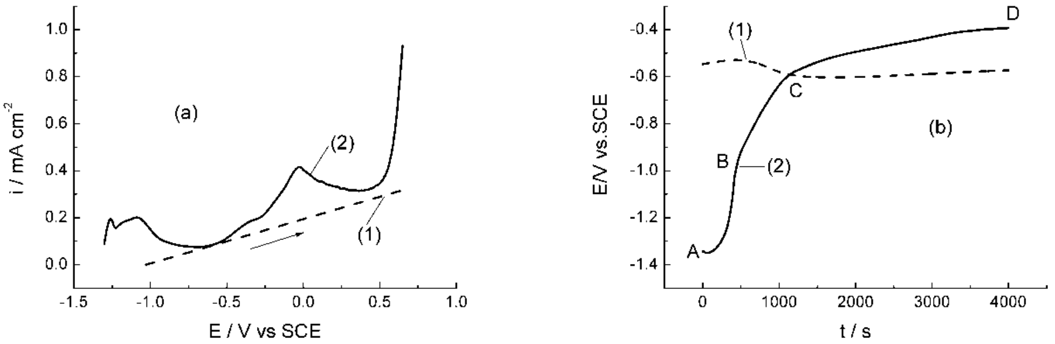

Fig.3. (a) Anodic polarization curves of the ZnMn wires in the solutions 4 (curve 1) and 5 (curve 2) listed in Table 1; (b) electrode potential transient during anodization of ZnMn wires grown on Cu/Au substrate (array shown in Fig.2) using anodic current density of 0.075 mAcm^{-2} in the solutions 4 (curve 1) and 5 (curve 2) listed in Table 1

We may interpret that the surface layer created initially by anodizing of ZnMn wires in the solution 4 (Fig.3a, curve 1) allows the transport of the cations and their chemical combination with OH^- ions at the interface with anodizing solution; as a result, an increase of the oxide layer thickness takes place during anodizing process. In the solution 5 (Fig.3a, curve 2), after a first oxide formation process a quasi-passive layer is obtained in a restricted region of electrode potentials (-0.75 ÷ -0.65V), with a small anodic current of electrolysis; at these potential values, the oxide layer should contain manganese oxide as MnO or Mn_3O_4 [12].

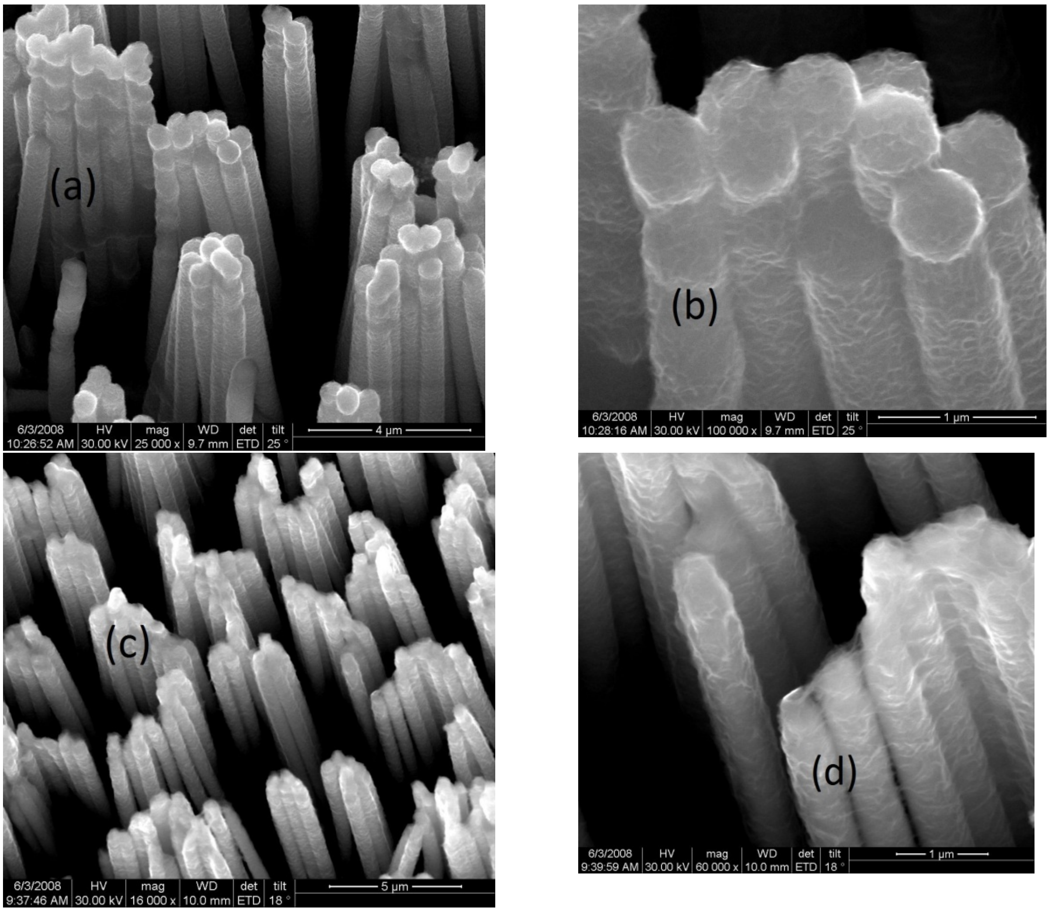

Fig.4. Morphology of the ZnMn alloy wires anodized for 4000 s at current density of 0.075 mAcm^{-2} in the solutions 4 (SEM images(a) and (b)) and 5 (SEM images (c) and (d))

Certainly, by polarizing to more anodic potentials, manganese oxides with manganese in a high oxidation state could be obtained. We noticed that the process of oxygen evolution begins at around 0.5 V potential. Fig. 3b shows the potential-time transients recorded during anodization of ZnMn alloy wires in solutions 4 and 5, at current density of 0.075 mAcm^{-2}. Anodizing in the solution 4, the initial potential of electrode is shifted towards negative potentials, whereas the surface of the wires is covered with a thin layer of oxide; afterwards, the electrode potential is slowly shifted to anodic potentials due to the increase of the thickness of oxide layer. In the solution 5 (Fig.3b, curve b) the transient can be divided into three regimes: initially, ZnMn wires are electrochemical oxidized and the formed oxide is fast dissolved (A-B region); at more anodically potentials a stable oxide layer on ZnMn wires is formed in contact with the zincate saturated aqueous solution (B-C region); then, a slightly increase of the thickness of the surface oxide layer could take place (C-D region).

SEM images of the ZnMn anodized for 4000 s in the two solutions, 4 and 5, are presented in the Figure 4. An aggregation process of the wires is observed after the anodization in both cases; moreover, the wires lost their definite form and their external part is covered with scales. According to the results of EDX measurements, the composition of the ZnMn wires anodized in solution 4, determined on the top of wires, comprises in atomic percents: Mn-22%, Zn-78%; a similar measurement for ZnMn wires anodized in the solution 5 indicated in atomic percents Mn-20% and Zn-80%. Formation of manganese-rich wires during anodization in the solution 4 indicates a ZnO dissolution process at the selected anodization current.

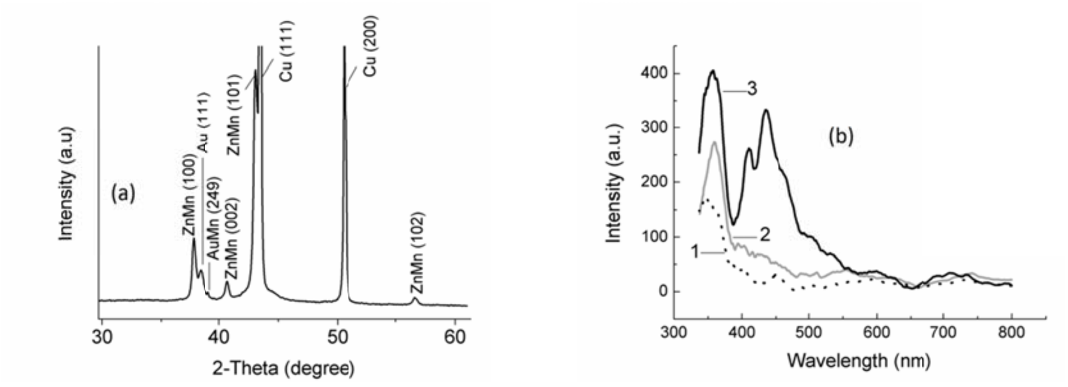

Fig.5. (a) XRD pattern of ZnMn wires anodized in the solution 4; (b) room-temperature photoluminescence spectra of submicron wire arrays of: 1– ZnMn alloy, 2- ZnMn alloy anodized at current density of 0.075 mAcm^{-2} in solution 5, 3- ZnMn alloy anodized at current density of 0.075 mAcm^{-2} in the solution 4

XRD analysis (Fig.5a) shows only ZnMn peaks originating from the metallic part (phase Zn2.92Mn1.08) of the wires, indicating that the formed structure on the external part of the wire consists in an amorphous phase.

The typical photoluminescence of ZnO is discussed in literature in terms of a dominant band in visible region (550-700nm) with other band in the UV region. The photoluminescence spectra of ZnMn metallic wires and of ZnMn wires anodized in the solution 4 and 5, respectively, are shown in Fig. 5b. Both spectra exhibit emissions at around 360 nm (excited at 325 nm); supplementary, the spectrum of ZnMn wires anodized in the solution 4 shows a violet/blue luminescence band in the range 410-460 nm. The origin of this band is not well understood but it seems that is related to a nonstoichiometric zinc oxide [13]. Results reported in the literature showed that manganese doping of ZnO does not change the peak positions in ZnO photoluminescence spectrum, but it is expected to cause a reduction in the intensity of the emissions [14]. We mention that according to our EDX data the anodization of ZnMn wires in the solution 5 produces an increase of manganese concentration in the oxidized wires. The corresponding photoluminescence spectra show a small UV emission and the absence of the visible emission band, suggesting that the surface oxide layer is also enriched in manganese ions [15]. The presence of a small emission in the photoluminescence spectrum of ZnMn wires could be due to formation of ZnO compound either during metallic wires preparation [10] or by oxidation of ZnMn wires in air.

4. Conclusions

We have presented our results about preparation of ZnMn alloy submicron wires by pulse electrodeposition and their anodization in two different solutions: a methoxyethanol solution containing sodium hydroxide and a potassium zincate aqueous solution, respectively. ZnMn alloy wires (having around 600 nm in diameter) prepared by pulse plating from a sulphate solution containing both zinc and manganese ions are monophasic (a Zn2.92Mn1.08 phase). Partial anodizing of ZnMn wires at current density of 0.075 $mAcm^{-2}$ in aqueous zincate solution led to formation of manganese-rich wires, due to ZnO chemical dissolution in the anodizing solution. SEM images and XRD analysis showed the presence of the oxide layer as an amorphous phase on the surface of the anodized ZnMn wires. An aggregation process of the wires was observed after the anodization in both solutions. The photoluminescence spectra of anodized ZnMn wires showed a small UV emission and the absence of the visible emission band which suggest that surface oxide layer also contains manganese ions.

Acknowledgements

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