ZnO:Mn SUBMICRON WIRES PREPARED BY ELECTROCHEMICAL SYNTHESIS

Mariana SIMA[1], Teodor VIŞAN[2], Marian SIMA[3], Eugeniu VASILE[4]

S-a investigat electrodepunerea în porii membranei de policarbonat a firelor de dimensiuni submicronice din ZnO dopate cu mangan din soluţii apoase conţinând Zn(NO3)2+Mn(NO3)2 prin voltametrie liniară şi spectroscopie de impedanţă electrochimică (EIS). Precipitarea semiconductorului ZnO:Mn în porii membranei folosite ca matrice a fost observată la un potenţial de circa –1.1 V/SCE. Circuitul electric echivalent utilizat pentru fitarea rezultatelor experimentale EIS a fost similar cu acela pentru caracterizarea sistemelor metal/film polimeric. Morfologia reţelelor de fire ZnO:Mn a fost evidenţiată prin microscopie electronică de baleiaj, iar conţinutul de Mn al probelor obţinute a fost determinat prin difracţie de raze X. Firele submicronice preparate la potenţial de -1.1V au compoziţia Zn0.97Mn0.03.

Electrodeposition of manganese doped ZnO submicron wires into polycarbonate membrane pores from aqueous solutions containing Zn(NO3)2+Mn(NO3)2 was investigated using linear sweep voltammetry and electrochemical impedance spectroscopy (EIS). The precipitation of ZnO:Mn semiconductor in the pores of membrane used as template was observed at a potential about -1.1V/SCE. The equivalent electrical circuit used for fitting experimental EIS results was similar to that for characterization of metal/polymer coating systems. Morphology of the ZnO:Mn wires arrays was observed by scanning electron microscopy, and the Mn content of the obtained samples was measured by X-ray diffraction analysis. The submicron wires prepared at a potential of -1.1V have a composition expressed by the formula Zn0.97Mn0.03.

Keywords: ZnO:Mn wires; electrodeposition; impedance spectroscopy

1. Introduction

The development of new miniaturized electronic and of optoelectronic devices for special applications requires a new generation of building blocks such as semiconductor nanowires or nanodots. For such applications, the template technique of electrodeposition has opened the possibility for preparation highly

[1] Researcher, Natl. Inst. of Mater. Phys., P.O. box MG 7, 077125, Magurele, Romania, msima@infim.ro
[2] Prof., Dept. Appl. Phys. Chem. & Electrochem., University POLITEHNICA of Bucharest, Romania
[3] PhD, researcher, Natl. Inst. of Mater. Phys., P.O. box MG 7, 077125 Magurele, Romania
[4] PhD, researcher, METAV-R&D Inst., Bucharest, Romania

ordered semiconductor nanowire arrays in a straightforward manner. Zinc oxide is a low-cost, non-toxic material with a wide band gap of ~3.37 eV and natural n-type electrical conductivity, having a wurtzite structure. Because of its optical, electrical and piezoelectrical properties, this semiconductor is used as photoanode in high efficiency dye-sensitized solar cells [1], as well as in various other applications as light-emitting diodes [2], lasers [3], field-emission devices [4], and chemical sensors [5]. It was shown that by replacing a fraction of cations of this host semiconductor material with other transition metal ions, a promising diluted magnetic semiconductor (DMS) material for spintronics applications could be obtained [6]. In DMS, apart from electron's charge degree of freedom, one uses the spin degree of freedom, a fact that can lead to a new class of devices and circuits.

The aim of the present paper was the investigation of electrochemical growth process of Mn doped ZnO submicron wires from nitrate aqueous solution, using linear sweep voltammetry and EIS techniques

2. Experimental

The solution used to investigate the electrodeposition process of manganese doped ZnO submicron wires contained 0.05 mol dm^{-3} $Zn(NO_3)_2$ + 0.1 mol dm^{-3} $Mn(NO_3)_2$ dissolved in bidistilled water. During the measurements, the temperature of the solutions was kept constant at 70 ^{0}C. For linear voltammograms measurements, the working electrode was a polycarbonate membrane (pore diameter 500 nm, pore density 10^8 cm^{-2}, membrane thickness 30 μm) covered with a copper/gold layer on one side, playing the role of cathode; its surface area was of 2 cm^2. The preparation and previous treatments of such membrane cathode was previously described [7]. EIS characterization of electrodeposition process of doped ZnO wires was made using similar polycarbonate membrane with a similar metallic film on one side; the surface area of this membrane electrode was of 1 cm^2. The electrochemical cell also contained a zinc foil (4 cm^2 surface area) as auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode.

Both linear voltammetry and EIS measurements were performed using a VOLTALAB 10 potentiostat digitally controlled by a PC computer. EIS tests were carried out in 10^{-1} Hz $\leq$ f $\leq$ 10^5 Hz frequency range with an *ac* voltage amplitude of ±5 mV, at a potential of -1.1 V/SCE. The impedance spectra were registered after 5 min deposition at potential -1.1 V of small segments of ZnO:Mn semiconductor in the pores of membrane used as template. These spectra were interpreted on the basis of equivalent electrical circuit using specialized fitting software, Zview 2.90c. The microstructures of deposits were imaged by scanning electron microscopy (SEM), using a FEI Quanta InspectF scanning electron

microscope equipped for chemical composition measurements with an EDX device.

3. Results and discussion

Characterization of doped ZnO electrodeposition process by linear voltammetry and SEM microscopy

The template method used in this work involves the precipitation of ZnO:Mn submicron wires or tubes in cylindrical pores of polycarbonate membrane having a thin metallic film on the bottom. Figure 1 shows the linear voltammetric curves recorded using a 0.05 mol dm^{-3} $Zn(NO_3)_2$ + 0.1 mol dm^{-3} $Mn(NO_3)_2$ solution. It may be observed in the first potential sweep (curve 1) a first cathodic process that starts at –0.4 V potential and exhibits a peak at potential values around -0.57 V.

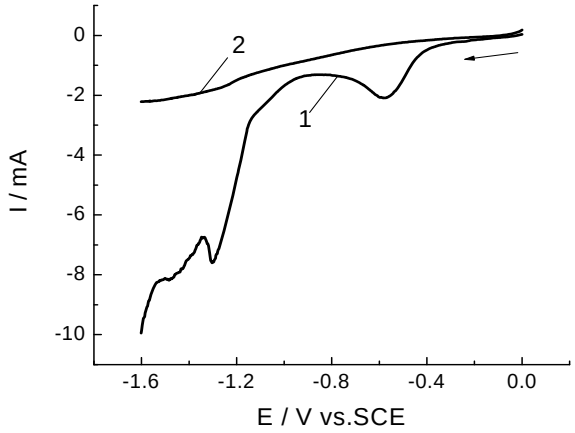

Fig.1. Voltammetric curves obtained for a Cu/Au/polycarbonate membrane electrode (2 cm^2 geometrical surface area) in the solution 0.05 mol dm^{-3} $Zn(NO_3)_2$ + 0.1 mol dm^{-3} $Mn(NO_3)_2$; scan rate 5 mV/s; t=70 ^{0}C. Curve 1-first sweep. Curve 2 was registered after deposition of a small segments of ZnO:Mn semiconductor (5 minutes deposition at -1.1 V) into the pores of membrane

It is well known that the nitrate ions are difficult to be directly reduced electrochemically in aqueous solutions [8] because of electrostatic repulsion between NO_3^- species and the cathode. However, it was observed that its reduction potential becomes more positive in the presence of a transition metal ion and it was supposed that the metal ion acts as an intermediate for the charge transfer from the electrode to the nitrate ion [9]. Also, it was suggested that the

reduction process of nitrate ions is correlated to the stability of the complexes formed by hydrolysis of metal ions in the solution [9, 10].

Consequently, we consider that this process corresponds to NO_3^- ion reduction on cooper/gold electrode, leading to the chemical process of oxide precipitation. The diminishing of the current after the maximum (within the potential range of -0.7 ÷ -0.9 V) may be attributed to the precipitation of zinc oxide that can introduce a supplementary electrical resistance in the circuit during the potential scan. This interpretation is also in full agreement with other authors' results [11] who showed that the electrochemical ZnO deposition from $Zn(NO_3)_2$ electrolyte involves an intermediate step which corresponds to the formation of hydroxide ions by reduction of nitrate species:

$$NO_3^- + 2\ e^- + H_2O \rightarrow NO_2^- + 2\ OH^- \quad (1)$$

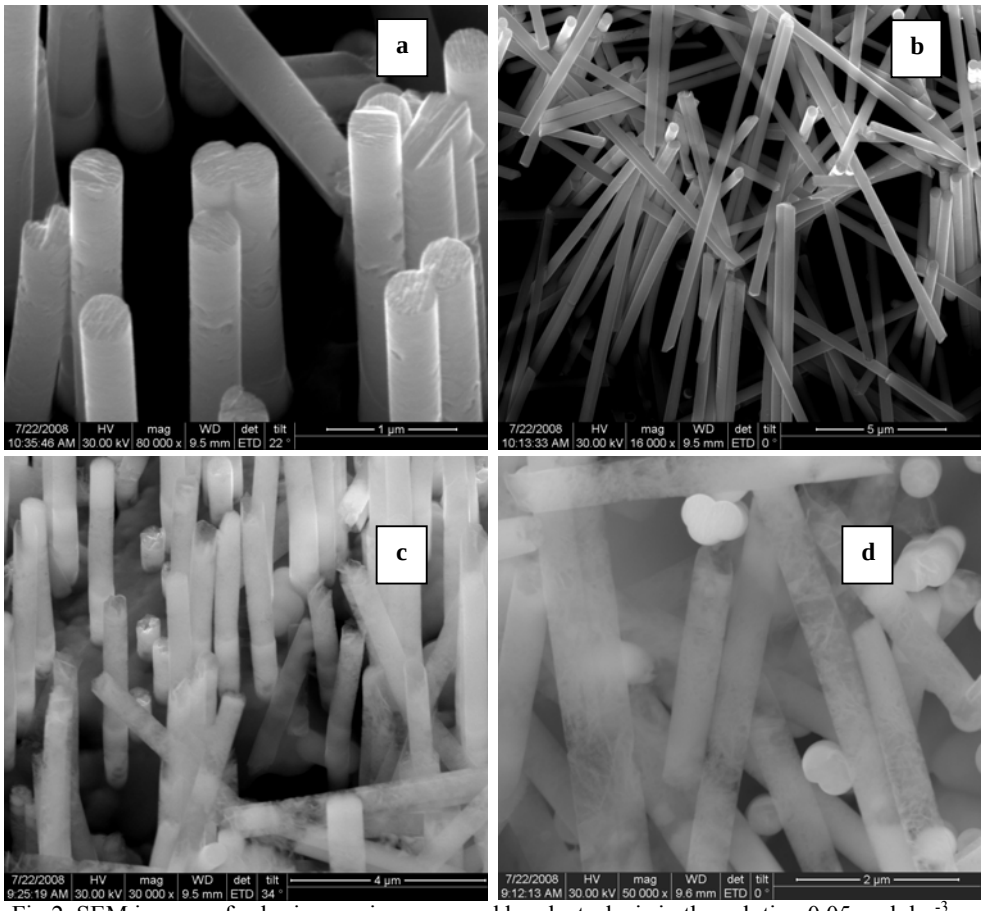

Fig.2. SEM images of submicron wires prepared by electrolysis in the solution 0.05 mol dm^{-3} $Zn(NO_3)_2$ +0.1 mol dm^{-3} $Mn(NO_3)_2$ at potentials: -0.95V (wires length: 15µm, pure ZnO, Figures a, b) and -1.1V (wires length: 6µm, Mn doped ZnO, Figures c, d)

The obtained hydroxide ions increase the local pH on the electrode surface, so that the solution pH can range to values till 10 [12], determining the precipitation of $Zn(OH)_2$. Zinc hydroxide participates in a subsequent step with the formation of a ZnO deposit, according to the following reaction scheme:

$$Zn^{2+} + 2\ OH^- \rightarrow\ Zn(OH)_2\ \rightarrow ZnO\downarrow\ +\ H_2O \qquad (2)$$

Indeed, in a separate electrolysis experiment we prepared the submicron wires at -0.95V electrode potential with high mechanical strength (Fig.2 a, b), and EDX measurements showed that they do not contain manganese species.

As Fig. 1 shows, the superposed reduction to metals waves of manganese and zinc ions are observed along the curve 1 around -1.15 V. Comparatively, the voltammogram recorded after previous electrodeposition of small segments of ZnO:Mn into the membrane pores (Fig. 1, curve 2) reveals only a small wave with a non-prominent peak at about -1.15 V, besides the main wave of nitrate reduction process.

The deposited metal seeds are unstable in the presence of hydroxyl ions obtained during nitrate reduction, and they convert into their hydroxides, that afterwards change in oxides. The observed peak at -1.35 V is due to suddenly occurrence of hydroxides onto the electrode surface. The chemical composition (at %) of segments prepared at -1.1 V is 97% Zn and 3% Mn, and it remains uniform over the length (around 6 μm) of the pores. The presence of manganese ions into ZnO matrix at this potential (near to manganese reduction potential) could be explained by the local increase of concentration of this ion at electrode surface. ZnO:Mn semiconductor grows initially as bars (submicron wires), but it is obtained subsequently as submicron tubes with walls of small thickness and granular structure. The morphology of these ZnO:Mn microtubes arrays is illustrated in Figures 2, c and d. As a general observation, the lower values of current along the curve 2 in Fig. 1 show that the rate of reduction process significantly diminished after previous deposition of a small ZnO:Mn segment into the membrane pores. This fact explains the semiconductor nature of submicron tubes.

Measurements of electrochemical impedance

Figures 3, a and b, show the Nyquist and Bode spectra obtained for Cu/Au/membrane electrode in nitrate solutions at -1.1 V potential. Both plots show two time constants, the first relating to a capacitive behavior typical of electrolyte/electrode interface (semicircle at high frequencies), and the second one referring to a limited diffusion process, due to the finite volume of the membrane pores (corresponding to a sloping line extended to low frequency).

By applying alternating current, it can be considered that the metal-polymer membrane electrode could behave like metal/protecting coating systems; these systems are frequently studied by electrochemical impedance spectroscopy [13]. Consequently, we suppose that the equivalent electrical circuit for the characterization of ZnO:Mn microtubes electrodeposition is expected to be similar to that used for metal/polymeric film electrode. The experimental results were fitted by the use of the equivalent electrical circuit shown in Fig. 4, corresponding to the obtained two time constants.

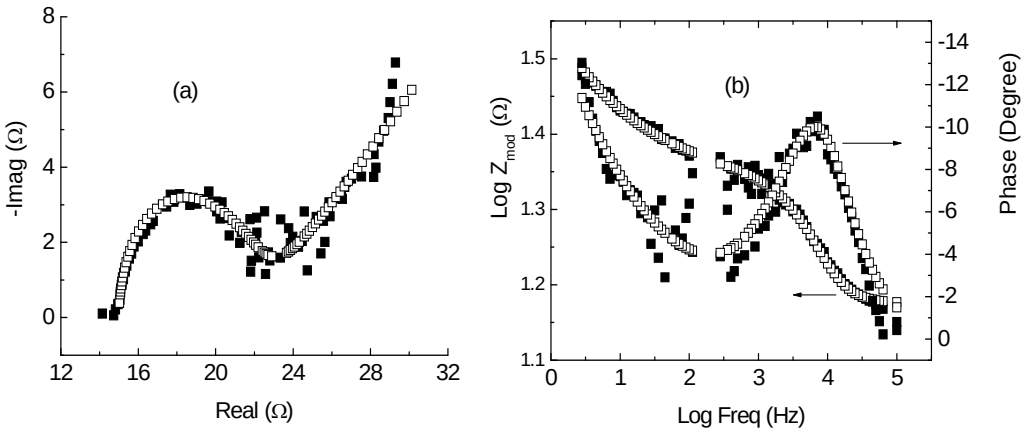

Fig. 3. Nyquist (a) and Bode (b) diagrams for Cu/Au/membrane electrode (1 cm^2 geometrical surface area) in solution 0.05 mol dm^{-3} $Zn(NO_3)_2$ + 0.1 mol dm^{-3} $Mn(NO_3)_2$ at -1.1 V; temperature 70 ^{0}C; ■■■- experimental data; □□□- fitting results

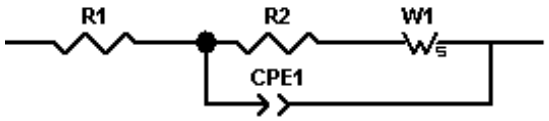

Fig. 4. The equivalent electrical circuit used to fit the impedance spectra from Figs. 3

Only the experimental data obtained in 2 Hz ≤ f ≤ 10^5 Hz frequency range were possible to be fitted. The resistive component R1 represents the ohmic contribution of electrolyte (ohmic resistance of solution). The first time constant is determined by the charge transfer resistance, R2, for nitrate ions reduction, connected in parallel with a double layer capacitance represented by a constant phase element, CPE1. The second time constant is described by the Warburg

impedance, W1, which represents the diffusion phenomena of NO_3^- ions into the membrane pores. Table 1 contains the values of equivalent circuit elements.

For an anomalous diffusion, in the restricted volume of the membrane pores we used the generalized finite Warburg element, proposed and justified by Macdonald [14] only as formula to fit the obtained data:

$$Z_W = R\,\frac{\tanh(i\tau\omega)^P}{(i\tau\omega)^P}, \tag{3}$$

where $i=\sqrt{-1}$, τ is the time constant associated with the diffusion process, ω is the angular frequency, R represents a diffusion impedance component, independent of the frequency, and P – an exponent taking values between 0 and 1. In the diffusion process interpretation, the time constant is correlated to layer thickness, L:

$$\tau = \frac{L^2}{D} \tag{4}$$

where D is the diffusion coefficient of ionic species.

Table 1

Values of the circuit parameters for Cu/Au/membrane electrode (1cm^2 geometrical surface area) in solution of 0.05 mol dm^{-3} $Zn(NO_3)_2$ + 0.1 mol dm^{-3} $Mn(NO_3)_2$ at -1.1 V; temperature 70 ^{0}C

Circuit element		ZnO:Mn (potential: -1.1 V)
R1, Ω		15
R2, Ω		6.6
W1	R, Ω	36.7
	τ, s	1.6
	P	0.37
CPE1	T, Ω^{-1} s^P	8.12×10^{-6}
	P	0.93

The generalized finite Warburg element with the impedance depicted by the equation (3) is an extension of another more common element, the finite length Warburg element, which is the mathematical solution of the one-dimensional diffusion equation of a particle. For this last element P = 0.5.

The ideal impedance spectrum for spatially restricted diffusion (the case P = 0.5) should show a straight line at an angle of 90^0 to the X axis at the low frequency limit, and a line in the semi-infinite diffusion region, with an angle to

the X axis of 45^0. However, this behavior is rarely observed for real systems, for which both mentioned angles are smaller. The equation (3), where P continuously varies between 0 and 1, was proposed in order to match these features. For the real systems, the presence of wide distribution of site energies produces a dispersion of time constants and implies a diffusion process that fundamentally differs from that described by Fick laws [15]. In our case, anomalous diffusion of the ions could be attributed to the membrane pores which dynamics is governed by thermally driven bending fluctuations [16].

Using the τ values for ZnO:Mn deposition (from the Table 1) in equation (4), and a value of membrane thickness L=30 μm, we estimated a diffusion coefficient value for NO_3^- ion in the working solution at 70 ^{0}C of 5.6×10^{-6} cm^2s^{-1}. Due to the diffusion within membrane pores, this value is smaller than D values usually obtained for inorganic ions in aqueous solutions.

The charge transfer resistance per unit area for NO_3^- ion reduction was calculated on the basis of R2 value from Table 1 and of the actual surface area of the membrane (pore diameter 500 nm, pore density 10^8 cm^{-2}) electrode; the obtained value was of 1.3 Ωcm^2, that means a value of around 10 $mAcm^{-2}$ (which is comparable to values from literature [17]) for exchange current density (taking the number of transferred electrons in the process, n = 2 (1)).

The double layer capacitance was described using a constant phase element, CPE1, due to the non-homogeneous chemical reactions on the changeable surface of the electrode. This is justified owing to the metallic hydroxide precipitation and its conversion in oxide, and also because the active centers on the working electrode surface might possess different activation energies. The impedance of this CPE component is described by the equation (5) [14]:

$$Z(CPE) = \frac{1}{T\ (i\omega)^P} \tag{5}$$

where the parameter T is associated with double layer capacity, and exponent P takes values between 0 and 1. The values obtained by experimental data fitting, T equals approximately to ten microfarads and P closed to unity, are suitable, reflecting the applicability of the chosen equivalent circuit.

It may be considered that the chemical step in the mechanism of the oxide formation on the electrode surface has a large enough reaction rate, so that any supplementary impedance does not appear in this system.

4. Conclusions

The results obtained by linear voltammetry and impedance measurements of submicron wires (tubes) electrodeposition are discussed in terms of the cathodic reduction of nitrate ion, as well as of the subsequent precipitation of Zn^{2+} and Mn^{2+} ions, as Mn doped zinc oxide into the pores of the polycarbonate membrane. The precipitation of ZnO:Mn semiconductor tubes in the membrane pores used as template was observed at the potential -1.1 V/SCE, close to manganese ion reduction potential, if a previous deposition of small segments (submicron wires) is performed.

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