

MANGANESE AND COPPER DOPED CdS NANOWIRE ARRAYS PREPARATION

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Manganese and copper doped CdS nanowires were obtained by the template technique in a two step process. In the first step metallic alloy CdMnCu nano and microwires were electrodeposited in ion track membranes with pore diameters in the range 150 nm – 2 µm. In the following step the resulted nanowires were anodized in a sodium sulphide alkaline solution. Electron microscopy results show participation of the whole metallic wire in the anodization process; manganese and copper doped CdS wires are obtained. The composition of micro and nanowires was determined by energy dispersive X-ray analysis.

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1. Introduction

One dimensional (1-D) semiconductor nanostructures exhibit novel optical and magnetic properties and they are key components in the fabrication of new type of devices. The use of both the spin and the charge of electrons in semiconductors is the challenge for storage and processing of information in electronic devices. Diluted magnetic semiconductors like CdS:Mn²⁺ nanorods are candidate materials for spintronic applications [1-3]. Apart from their potentials electronic applications, these semiconductor nanowires are interesting for possible use in luminescent devices [4-7]. The template synthesis is a simple and versatile method for preparing nanostructural material [8-12], which entails synthesizing the desired material within the pores of a nanoporous template membrane. The electrochemical synthesis in templates has been taken as one of the most efficient methods in controlling the growth of nanowires because the growth is controllable almost exclusively in the direction normal to the surface.

In this paper, we will report our work on the electrochemical preparation of CdS:Mn²⁺:Cu⁺ nanowire arrays into the pores of nuclear track etch polycarbonate membrane.

2. Experimental

CdS:Mn²⁺:Cu⁺ nanowires were synthesized in two steps. The first step consisted in the electrochemical deposition of CdMnCu alloy nanowires. The second step was the anodization of the alloy micro and nanowires in a sodium sulphide alkaline solution. The synthesis of metallic wires was realized both in 30 µm thick polycarbonate membranes (obtained in GSI Darmstadt by irradiating the polymer foils with swift heavy ions and chemical etching) with pore diameter of 1.5 µm and pore density of 10⁶ cm⁻² and in 6 µm thick commercial polycarbonate membranes (Millipore), pore diameters 150-200 nm and pore density 10⁸ cm⁻².

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In order to perform the electrochemical preparation of micro and nanowires, a metal layer was deposited on one side of the membrane: for the thicker membranes a gold layer was sputtered on one side while for the thinner ones nickel was chemically deposited.

The membranes were clamped in an electrochemical cell with the pores exposed to the growth solution. A cadmium counter electrode and a SCE (saturated calomel electrode) reference electrode were used for the deposition. The anodizing process took place in the same arrangement this time being employed a platinum counter electrode.

Electrochemical studies on a platinum electrode were carried out in order to find the deposition conditions for the CdMnCu alloy and for the preparation of the doped cadmium sulphide compound. The deposition solutions of thin films of Cd, Mn and Cu onto the platinum electrode are presented in Table 1. For the deposition of the alloy in the desired ratio between the constituents a mixture of the three solutions was employed: 3 parts (volume) of the Cd ions solution, 12 parts Mn^{2+} solution and 0.04 parts Cu^{2+} solution. The deposition potential was -0.9 V versus SCE. A guide for selecting the deposition conditions and solution were the voltammetric curves of the individual processes for each metal in the solutions presented in Table 1 (Fig. 1).

Table 1. Deposition solutions for Cd, Mn and Cu.

Cd²⁺ solution	
CdSO ₄ 8/3 H ₂ O	1.4 M
(NH ₄) ₂ SO ₄	1 M
pH=3	
Mn²⁺ solution	
MnSO ₄ H ₂ O	0.59 M
(NH ₄) ₂ SO ₄	1 M
pH=3	
Cu²⁺ solution	
CuSO ₄ 5H ₂ O	0.8 M
(NH ₄) ₂ SO ₄	1 M
pH=3	

CdMnCu alloy anodization was performed in a solution containing $5 \times 10^{-2}\text{ M}$ Na₂S, 1M NaOH by scanning the potential in the range: -1.1 to 1.3 V/SCE . The electrochemical processes were performed with a potentiostat/galvanostat controlled by a PC. All the measurements were performed at room temperature.

Sulphide nanowires were studied by electron microscopy and their composition was determined by energy dispersive X-ray analysis (EDX).

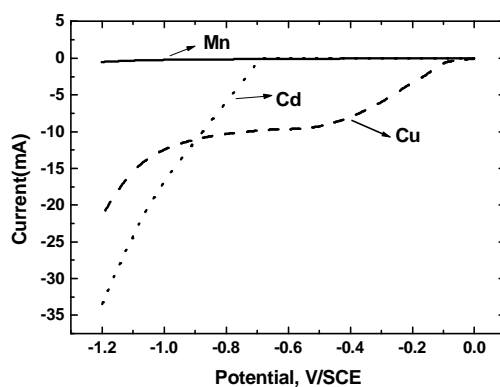


Fig. 1. Voltammetric curves for the deposition of thin films of Cd, Mn and Cu on platinum substrate (electrode surface 0.065 cm^2) from acid solutions of the corresponding ions (Table 1); potential scanning rate 5 mV/s

3. Results and discussion

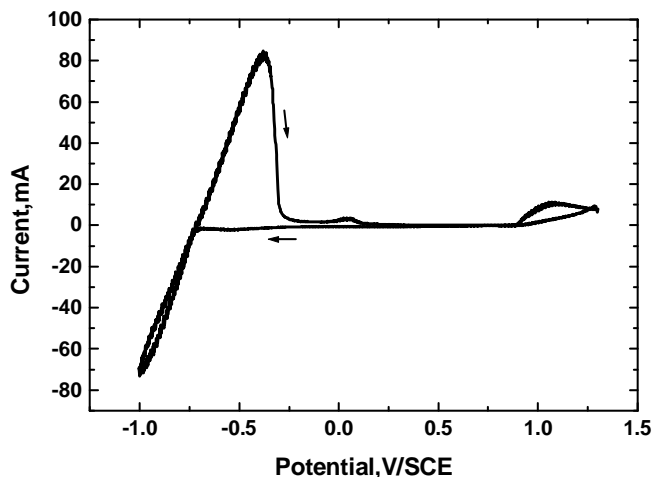


Fig. 2. Cyclic voltammogram of platinum electrode (1 cm^2) in the synthesis solution of the CdMnCu alloy; scan rate 50 mV/s.

Reduction process of Cu^{2+} ions (which takes place in two steps) in the chosen solution starts (Fig. 1) at about -0.06 V/SCE , for Mn^{2+} at about -1 V/SCE and for Cd^{2+} at -0.7 V/SCE . Taking into account the deposition currents (Fig. 1) at a potential which allows the codeposition of the Cd, Mn, Cu metals (-0.9 V/SCE) the composition of the synthesis bath for the CdMnCu alloy was approximated in order to obtain cadmium as the base component and the other two metals representing less than 10% of the final alloy. In accord with the cyclic voltammogram in Fig. 2 the deposition process of the CdMnCu alloy begins at about -0.7 V/SCE . Cadmium is dissolved at a potential of -0.58 V/SCE and copper at -0.05 V/SCE ; the process at $+1.06 \text{ V/SCE}$ was attributed to the formation of a manganese oxide layer on the platinum electrode. The electrodeposition of CdMnCu alloy on a platinum electrode at a potential of -0.9 V/SCE produces a film without rugosity with the composition (atomic percents): 92.76 Cd, 3.27 Mn and 3.9 Cu.

In Fig. 3, curve 1 is presented the current as a function of time for the deposition of the alloy on a platinum electrode at the -0.9 V/SCE potential. It can be noticed initially a decrease of the deposition current correlated with the formation of the growth centers; the subsequent increase of current is due to the extending in electrode area by deposition of metallic layer.

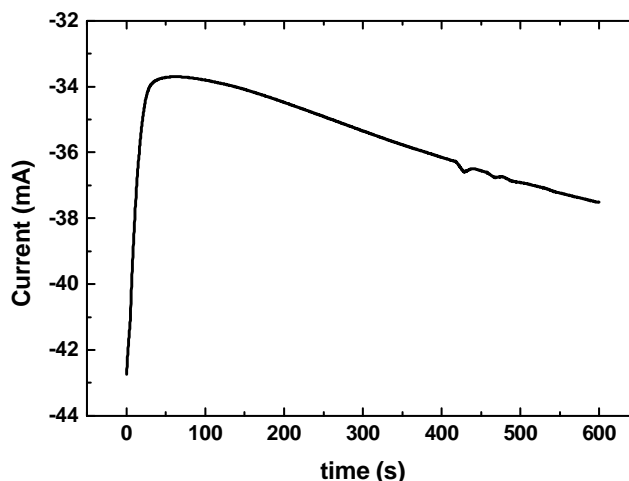
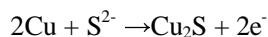


Fig. 3. Current time plot for the deposition of the CdMnCu alloy on platinum substrate (1 cm^2) at constant potential (-0.9 V/SCE).

For the synthesis of the $\text{CdS:Mn}^{2+}:\text{Cu}^+$, the metallic alloy was anodized in an alkaline sodium sulphide bath. This process allows the introduction of copper as a monovalent ion [13] in the sulphide material. In order to obtain the compound by anodic oxidation in the sulphide bath the metallic ions should present a high mobility in the doped semiconductor phase. Copper anodization in a sulphide bath takes places according the general reaction:



Literature data [14] indicate a high mobility of the Cu^+ ion through the layer of Cu_2S ($D=10^{-10} \text{ cm}^2/\text{s}$) and this is the reason that the electric conductivity of this semiconductor is almost as high as for a metal ($10^2 \Omega^{-1}\text{cm}^{-1}$ at 25°C [15]). The ion diffusion through the CdS and MnS layers is more difficult, the anodic processes having as a result the passivation of the metallic surface (Fig. 4).

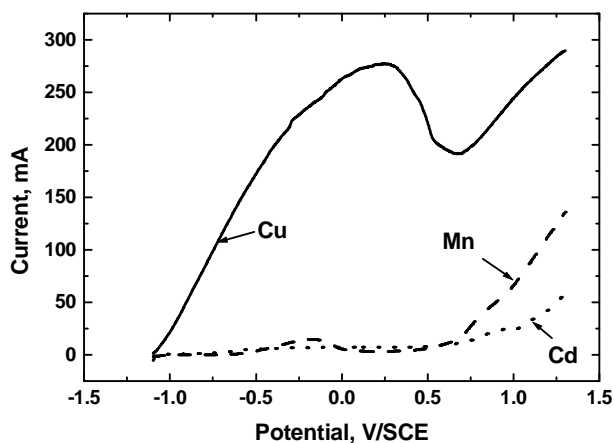


Fig. 4. Anodization of cadmium, manganese and copper deposited on a platinum electrode (1 cm^2) in a solution containing $5 \times 10^{-2} \text{ M Na}_2\text{S}$, 1 M NaOH for a potential scan in the range -1.1 V/SCE to 1.3 V/SCE ; scanning rate 50 mV/s .

The anodization process of the alloy on a platinum support is presented in the voltammogram plotted in Fig. 5. In the first cycle the characteristics of Cd, Mn and Cu anodization can be observed. In the following cycles the anodization current decreases significantly, at 1.1 V/SCE a new process appears which we attribute to the sulfide layer breaking; the increase of current in a sharp manner can be a support for this estimation.

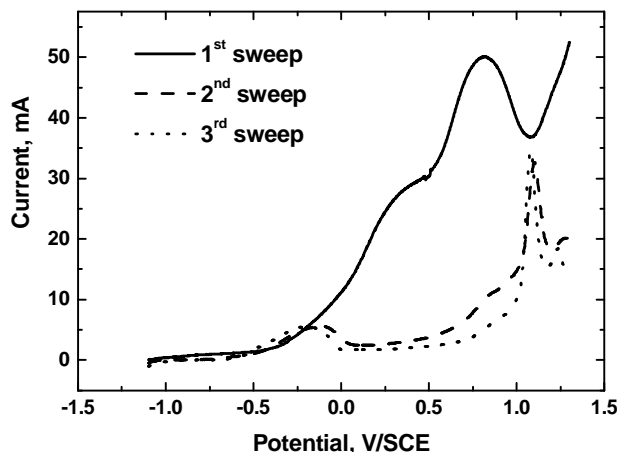


Fig. 5. Anodization of CdMnCu (1 cm^2) in an aqueous solution containing $5 \times 10^{-2} \text{ M Na}_2\text{S}$, 1 M NaOH ; potential scanning rate 50 mV/s .

Alloy deposition in polycarbonate membranes pores (Fig. 6) takes place somehow differently when compared to the layer deposition on the platinum electrode; after an initial transient, the current decreases in a process of formation of the metallic nuclei; the gradual increasing corresponds to the growth of nanowires in polycarbonate template.

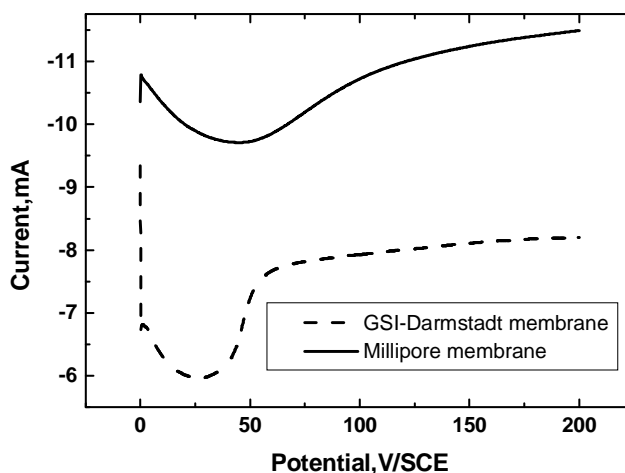


Fig. 6. Deposition current of the metallic alloy wires as a function of time (-0.9V/SCE).

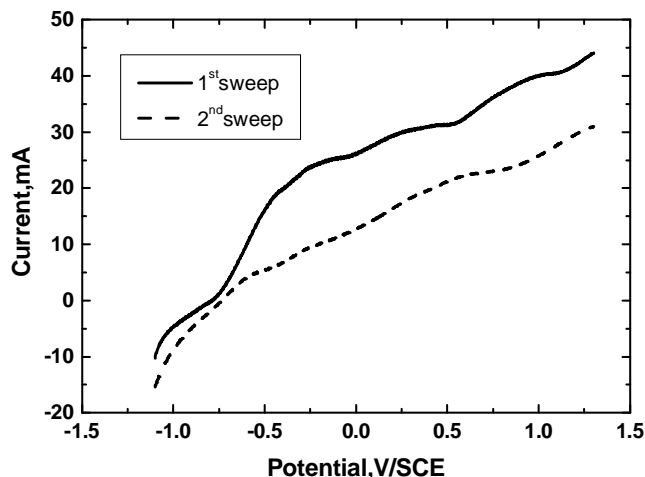


Fig. 7. CdMnCu wires anodization in the GSI-Darmstadt membrane in a solution containing $5 \times 10^{-2} \text{M Na}_2\text{S}$, 1M NaOH, potential scan in the range -1.1V to 1.3V; scanning rate 50 mV/s (membrane surface 1 cm^2).

The current increase due to the complete pore fill is sharper in the case of the GSI membrane when compared to the Millipore one revealing a more uniform growth of the wires and a narrow distribution of dimensions. The Millipore membrane growth current is larger due to the smaller thickness and higher pore density.

Alloy wires anodization plotted in Fig. 7 follows in the first cycle the similar steps as for the thin film deposited on a platinum substrate. Although in the second cycle the current decreases, we assume that the process takes place on the whole surface of the wires due to the penetration of the alkaline solution in the pores around the metallic wire. The anodization current decrease in the following cycles is not as large as in the case of the film and this is explained by ion diffusion process from solution to the metallic wires surface. Due to the small thickness of the wires and its large surface all the metallic wire is anodized.

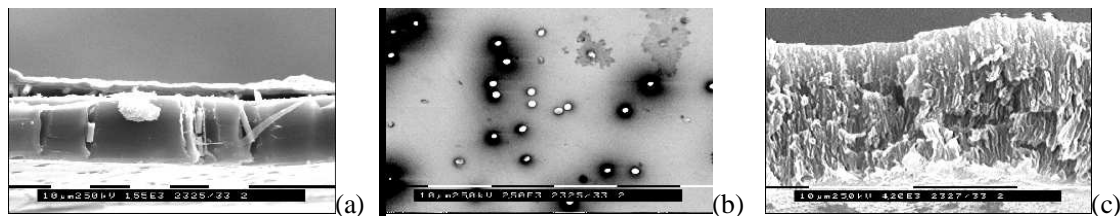


Fig. 8. SEM image of CdS: Mn²⁺: Cu⁺ wires prepared in the GSI membranes, (a - fractured cross section, b - image of the filled membrane surface) and Millipore membrane (c - fractured cross section).

SEM images allow the observation of the CdS: Mn²⁺: Cu⁺ wires (Fig. 8). Homogenous wires can be observed proving the participation of the whole wire at the anodization process. The sulphide wires composition was measured by energy dispersive X-ray analysis in a fracture of the membrane. The result indicates an almost stoichiometric compound containing in atomic percents: 52.18 S, 36.39 Cd, 7.74 Mn and 3.69 Cu.

4. Conclusions

Manganese and copper doped CdS nanowire arrays were prepared in a two steps process. In the first step we prepared micro and nanowire arrays of CdMnCu alloy using potentiostatic deposition in polycarbonate ion track membranes from acid solutions. For the synthesis of the CdS:Mn²⁺:Cu⁺, the metallic alloy was anodized in a solution containing 5×10^{-2} M Na₂S, 1M NaOH, scanning the potential in the range -1.1V to 1.3V/SCE. The metallic alloy wires participate with the whole surface at the anodization process. The obtained doped semiconductor nanowires show a nearly stoichiometric composition as resulted from the EDX measurements.

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