

PREPARATION OF METAL CHALCOGENIDES SEMICONDUCTOR NANOWIRES AND MICROTUBES

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Abstract. Recently, a great deal of attention has been paid to the fabrication of highly ordered nanowire arrays because of their fundamental importance and potential applications. We fabricated CdS:Mn²⁺:Cu⁺ nano and microwires and PbTe and PbSe nanowires and microtubes using electrochemical deposition and template method. The morphology of nanowires and microtubes was observed by scanning electron microscopy and the composition of these semiconductor nanostructures was measured by energy dispersive X-ray analysis (EDX).

Key words: template synthesis, electrodeposition, semiconductor nanowires and microtubes.

1. INTRODUCTION

The template synthesis is a simple and versatile method for preparing nanostructural material [1–4]. This method consists in filling the pores of a membrane with a certain material, which adopts the exact shape of the hosting pore. Two templates are mostly employed: anodic alumina prepared by anodizing aluminium and etched ion track membranes prepared by heavy ion irradiation and chemical etching. This latter technique for preparation of membranes has the advantage that each projectile creates an individual damage trail of a few nanometers in diameter. The length of the resulting ion track is determined by the ion energy and can reach several hundred μm . By chemical etching, tracks can be enlarged to pores of different sizes and extremely high aspect ratios (up to 10^4). Moreover, many materials can be structured such as, for example, polymers (*e.g.*, Polyethylenetereftalate, Polyimide and Polycarbonate) and inorganic crystals such as mica, glass or quartz. Thus, by electrochemical and chemical deposition in etched ion track membranes, metallic and semiconducting structures with lengths up to tens of micrometers and diameters down to several nanometers have been prepared. 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.

One dimensional (1-D) semiconductor nanostructures exhibit novel optical and magnetic properties and they are key components in the fabrication of new types 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 [5–7]. Apart from their potentials electronic applications, these semiconductor nanowires are interesting for possible use in luminescent devices [8–10]. PbTe and PbSe are recognized as thermoelectric materials; recently, the topic of size effects of the thermoelectric materials has become important in thermoelectricity as enhancements of the dimensionless figure of merit, ZT, for low dimensional structures have been reported [11]. On the other hand, according to scaling factors, the attractive idea in the manufacturing of a thermoelectric microdevice is to increase specific power (W/cm²) by reducing the size of the thermoelectric elements, maintaining the same aspect ratio of elements in a larger thermoelectric device.

This paper presents our recent results in the preparation and characterization of doped CdS, PbTe and PbSe nanowires and nanotubes.

2. EXPERIMENTAL

Polycarbonate (Makrofol N, Bayer) foils with a thickness of 30 µm are used as templates. The foils are irradiated with swift heavy ions (*e.g.*, Au 11.4 MeV/nucleon specific energy). The fluences used for irradiation are in the range 10⁶ to 10⁷ ions/cm².

Next, the samples are exposed to UV radiation for one hour. This sensitization treatment improves the track etch selectivity (*i.e.*, higher aspect ratios, smaller statistical distribution of etching rate and thus of final dimensions of etched pores). The etching is performed in aqueous NaOH solutions with addition of methanol, either by completely dipping the irradiated foils into an etching pot in the case of cylindrical pores, or by exposing only one side of the membrane to the etching solution after inserting the foil in an electrolytical cell consisting of two chambers. The two parameters which are important for the shape of the resulting pore are the bulk etch rate (the etch rate of the non-irradiated material) and the track etch rate, the etch rate along the ion track. Cylindrical pores were obtained for high track etch rate to bulk etch rate ratios. The diameter of the resulting pores is in direct proportion with the etching time. For cylindrical pores, the etching solution contains 90% 5 M NaOH and 10% methanol and the temperature is 50°C. The choice of the etching conditions was made based on previous experiments.

A thin nickel or gold electrode film, which will later play the role of the cathode, was deposited on one side of the membrane by sputtering; this film was

reinforced by chemical or electrochemical deposition of copper. Subsequently the membranes were clamped in an electrochemical cell with the pores exposed to the growth solution and the growth was performed. The electrochemical deposition of semiconductor compounds into the pores was accomplished with a potentiostat/galvanostat connected to a computer.

After the electrodeposition process the polymer membrane was dissolved in CH_2Cl_2 . The nanorods were imaged by scanning electron microscopy and their composition was determined by energy dispersive X-ray analysis (EDX).

3. RESULTS AND DISCUSSION

CdS:Mn²⁺:Cu⁺ NANO AND MICROWIRES

Doped CdS wires were synthesized in two steps. The first step consisted in the electrochemical deposition of CdMnCu alloy nano and microwires (Fig. 1). The wires were obtained in two types of ion track polycarbonate membranes: a 30 μm thick membrane with pore diameters of 1.5 μm , obtained at GSI Darmstadt and commercial filtration membranes (Millipore) with thickness of 6 μm and pore diameters of 150–200 nm. The second step was the anodization of the metallic micro and nanowires in a sodium sulphide alkaline solution (Fig. 2). Metal deposition in polycarbonate membranes pores takes place somehow differently when compared to the layer deposition on the platinum electrode; after an initial transient, the current decreases in a polarization process; the gradual increasing corresponds to the growth of nanowires in polycarbonate template.

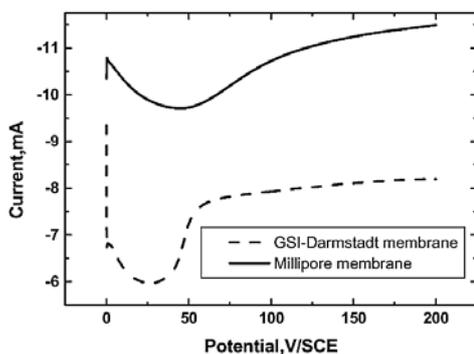


Fig. 1 – Deposition current of the metallic alloy wires as a function of time (at -0.9 V/SCE). The solution for preparation of CdMnCu alloy contains 0.28 M CdSO_4 , 0.47 M MnSO_4 , 0.0021 M CuSO_4 and 1 M $(\text{NH}_4)_2\text{SO}_4$; pH=3.

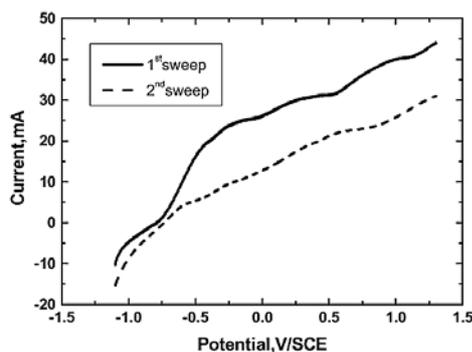


Fig. 2 – CdMnCu wires anodization in the GSI-Darmstadt membrane in a solution containing 5×10^{-2} M Na_2S , 1 M NaOH , potential scan in the range -1.1 V to 1.3 V; scanning rate 50 mV/s (membrane surface 1 cm²).

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. SEM images allow the observation of the $\text{CdS} : \text{Mn}^{2+} : \text{Cu}^+$ wires (Fig. 3). Homogenous wires can be observed proving the participation of the whole wire in 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.

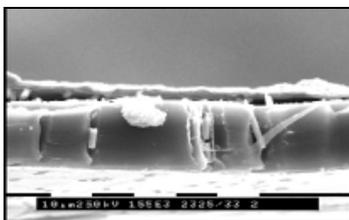


Fig. 3 – SEM image of $\text{CdS} : \text{Mn}^{2+} : \text{Cu}^+$ wires prepared in the GSI membranes (fractured cross section).

PbTe AND PbSe NANOWIRES AND MICROTUBES

PbTe and PbSe semiconductor compounds were electrodeposited using acid solutions [5, 6], containing 0.1 M HNO_3 , 0.05 M $\text{Pb}(\text{NO}_3)_2$, 0.001 M TeO_2 and, respectively, 0.1 M HNO_3 , 0.05 M $\text{Pb}(\text{NO}_3)_2$, 0.001 M H_2SeO_3 . We deposited PbTe from this acid solution in the membrane pores at potential -0.345 V/SCE (Fig. 4). A typical morphology of these PbTe nanowires and microtubes is shown in the SEM image in Fig. 5.

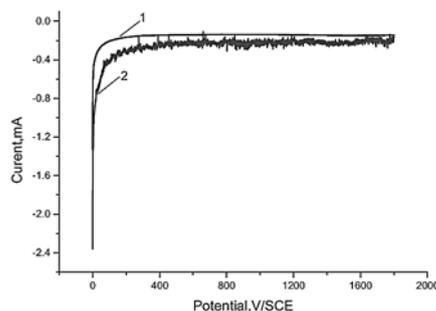


Fig. 4 – PbTe deposition into the pores of two polycarbonate membranes (pores diameter – $1.5 \mu\text{m}$, pores density – $10^6/\text{cm}^2$, membrane surface area – 1 cm^2) at a potential of -0.345 V/SCE .

It is shown that PbTe nanowires and microtubes have uniform diameters. After the dissolution of the membrane the thicker rods and tubes are still standing and their length is equal to the thickness of the foil.

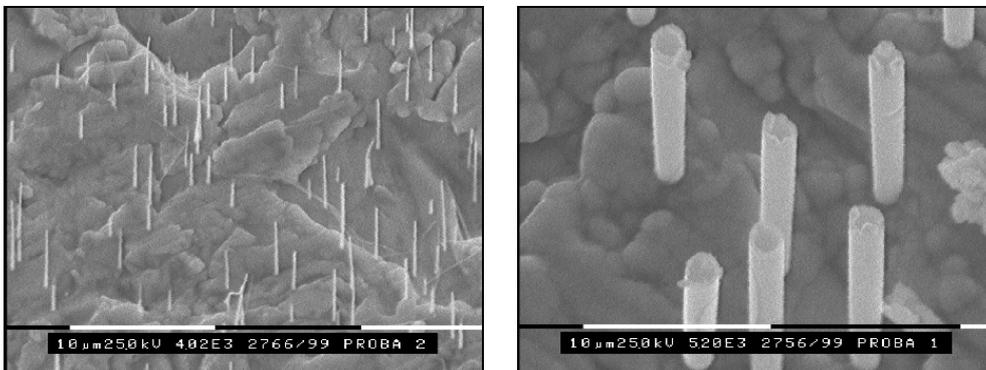


Fig. 5 – SEM images of PbTe nanowires (250 nm diameter) (*left*) and microtubes (1.5 μm diameter) (*right*) prepared by potentiostatic electrodeposition in track-etch membrane at -0.345 V/SCE.

The EDX measurements showed in atomic percent, a Pb/Te ratio of 1.13.

PbSe was deposited at -0.3 V/SCE into the micropores of a polycarbonate membrane and the SEM images of obtained nanowires and microtubes arrays are shown in Fig. 6.

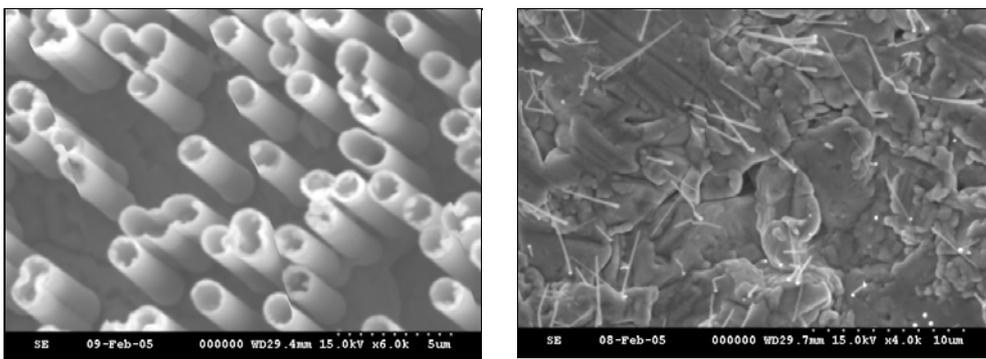


Fig. 6 – SEM images of an array of standing PbSe tubes 1.5 μm diameter (*left*) and of broken nanowires (wire diameter 250 nm) (*right*) prepared by potentiostatic deposition at -0.3 V/SCE.

Nanowires and microtubes of PbSe show a small excess of Se compared with the stoichiometric composition of this compound (EDX measurements).

4. CONCLUSIONS

Semiconductor nanowires prepared by the template method open the possibility of fabricating functional structures as temperature detectors, thermoelectric devices or photodiodes. Using the template method we prepared

CdS : Mn²⁺ : Cu⁺ micro and nanowires and PbTe and PbSe nanowires and microtubes. SEM images showed the preparing of homogeneous CdS : Mn²⁺ : Cu⁺ wires by CdMnCu alloy anodization; also we observed PbTe and PbSe nanowires and microtubes having uniform diameters and their length equal to the thickness of the polycarbonate membrane. The EDX measurements indicated the synthesis of almost stoichiometric compounds.

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