

## METAL CHALCOGENIDE SEMICONDUCTOR NANOWIRES

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In the last few years the field of nanowires increased dramatically especially due to the wide range of possible applications. The present paper deals with the preparation and study of metal chalcogenide semiconductor nanowires. CdS, CdTe and PbSeTe nanowires were obtained by electrochemical deposition in nanoporous ion track membranes. Scanning electron microscopy (SEM) was employed for observation. Energy dispersive X-ray analysis (EDX) was used for composition measurements. CdS photoluminescence was measured for both pure and doped nanowires.

*Keywords:* Nanowires, Template method, CdS, CdTe, PbSeTe, SEM, EDX, Photoluminescence

### 1. Introduction

The large interest in nanowires is based on their promising applications in different fields of the industry and as a tool for studying mesoscopic processes. During the last decades, the fast technological developments, promoted mainly by the microelectronics industry have led to a progressive miniaturisation of electronic devices. Though the resolution limit of the well-established production techniques such as e.g. electron-beam lithography is in the sub micrometer range, new structuring and assembly techniques have to be developed when nanometer dimensions are required. Up to now, several techniques have been used to produce nanowires with dimensions below 100 nm, for instance, by surface step decoration, laser assisted catalytic growth and template replication [1-4].

The template technique 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 anodising 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  $\mu\text{m}$ . 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 were obtained.

Metal chalcogenide semiconductors nanowires are of particular interest for several reasons. First, II-VI semiconductors present a broad range of band-gaps (from 0.15 eV in HgTe to 3.68 eV in ZnS). Second, most of them present direct energy gaps, which makes them particularly important for electro-luminescence devices such as e.g. light emitting diodes and lasers. Third, these semiconductors can be electrochemically deposited from aqueous solutions. The deposition process on macroscopic electrodes has been extensively studied in the last decades, driven by the large

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amount of applications that II-VI and IV-VI semiconductor devices have nowadays. Examples are the use of CdTe in a broad range of optoelectronic devices such as infrared, X-ray and gamma ray detectors, the investigations of CdTe/CdS systems as a good alternative to silicon solar cells, and the use of ZnSe to prepare light emitting or laser diodes in blue band. Moreover, these semiconductor compounds form solid solutions over a considerable range of compositions, and even better control over various properties and structural changes may be achieved in ternary semiconductors. The band gap and lattice parameters of the compounds can be varied continuously by changing the composition. An important example of this class is  $\text{Hg}_x\text{Cd}_{1-x}\text{Te}$ , (MCT) well established as an important material for infrared detectors and imagers.

The present paper is a review of our results in preparation of PbSeTe [5], CdS [6,7] and CdTe [8] nanowires. Doped CdS nanowires were also prepared, and the dependence of photoluminescence properties on doping was studied.

## 2. Experimental

Polycarbonate (Makrofol N, Bayer) foils with a thickness of 30  $\mu\text{m}$  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  $10^6$  to  $10^7$  ions/ $\text{cm}^2$ . 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 was 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/bulk etch rate ratios.

The diameter of the resulting pores is direct proportional to the etching time. For cylindrical pores, the etching solution contains 90% 5M NaOH and 10% methanol and the temperature is 50  $^\circ\text{C}$ . The choice of the etching conditions was made based on previous experiments.

A thin 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 carried out.

After the electrodeposition process the polymer membrane was dissolved in  $\text{CH}_2\text{Cl}_2$ . The nanorods were imaged by scanning electron microscopy, and their composition was determined by energy dispersive X-ray analysis (EDX).

## 3. Results and discussion

### a) PbSeTe nanowires

$\text{PbSe}_{1-x}\text{Te}_x$  was electrodeposited using an acid solution, containing 0.1M  $\text{HNO}_3$ , 0.05M  $\text{Pb}(\text{NO}_3)_2$ , 0.001M  $\text{H}_2\text{SeO}_3$  and 0.0006M  $\text{TeO}_2$ . In Fig.1 are presented comparatively the cyclic voltammograms of both Pt and copper /membrane electrodes in the synthesis solution. We noticed that the process of Pb, Se, Te ternary codeposition from the above solution starts at -0.1 V and shows a maximum current at -0.5V/SCE. The presence of Pb, Se, Te elements in the corresponding deposit is proved by voltammetric maxima at -0.3, 0.3 and 0.9V/SCE, respectively, on the anodic branch. Using a copper/membrane electrode as working electrode a similar process in the same

potentials range was evidenced. Moreover, on this cyclic voltammogram appears the anodic behavior (the dissolution, mainly) of copper electrode deposited on one side of polycarbonate membrane.

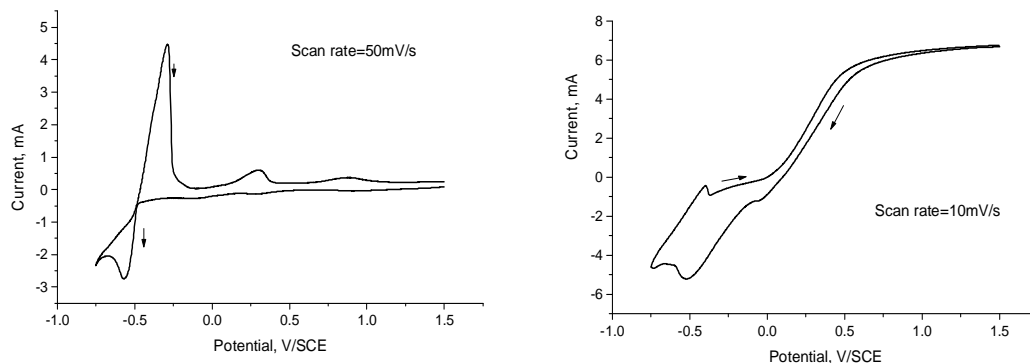


Fig. 1. Cyclic voltammograms of platinum electrode ( $S=0.065 \text{ cm}^2$ ) (left side) and copper/membrane electrode ( $S=0.8 \text{ cm}^2$ ) (right side) in the solution containing  $0.1 \text{ M HNO}_3$ ,  $0.05 \text{ M Pb(NO}_3)_2$ ,  $0.001 \text{ M H}_2\text{SeO}_3$  and  $0.0006 \text{ M TeO}_2$ ; the diameter of membrane pores is  $100 \text{ nm}$  and pore density is  $10^8 \text{ cm}^{-2}$ .

The micrographs showing the morphology of  $\text{PbSe}_{1-x}\text{Te}_x$  microtubes and nanorods are presented in Fig. 2 and Fig. 3, respectively. The composition of  $\text{PbSe}_{1-x}\text{Te}_x$  nanostructures was determined by ED technique and it is expressed by  $x=0.37$  for  $\text{PbSe}_{1-x}\text{Te}_x$  compound prepared at  $-0.337 \text{ V/SCE}$ .

The growth of microtubes instead of nanorods can be attributed to the presence of pores with large diameter in the used template and, consequently, to the larger deposition current which appears at nanotubes building.

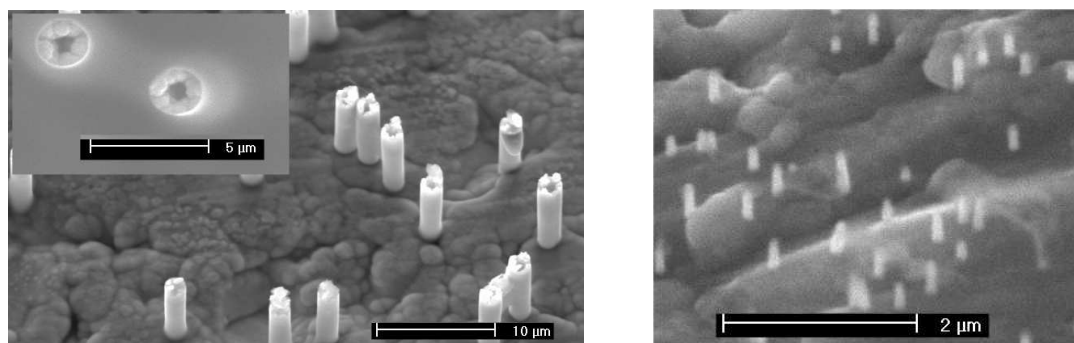


Fig. 2. SEM images of  $\text{PbSe}_{1-x}\text{Te}_x$  microtubes and nanowires prepared by potentiostatic electrodeposition in ion track membranes at  $-0.337 \text{ V/SCE}$ : (a) microtubes deposited in  $2000 \text{ nm}$  diameter pores; (b) nanowires deposited in  $100 \text{ nm}$  diameter pores

#### b) CdS nanowires

Pure and doped CdS nanowires were synthesized in two steps. The first step consisted in the electrochemical deposition of the metal nanowires (Cd nanowires in the case of pure CdS and CdMnCu alloy nanowires in the case of  $\text{Mn}^+\text{Cu}^+$  doped CdS nanowires). The second step was the anodization of the metallic micro and nanowires in a sodium sulphide alkaline solution.

Electrochemical studies on a platinum electrode were carried out in order to find the deposition conditions for the metallic alloy and for the preparation of the pure and doped cadmium sulphide compound.

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.

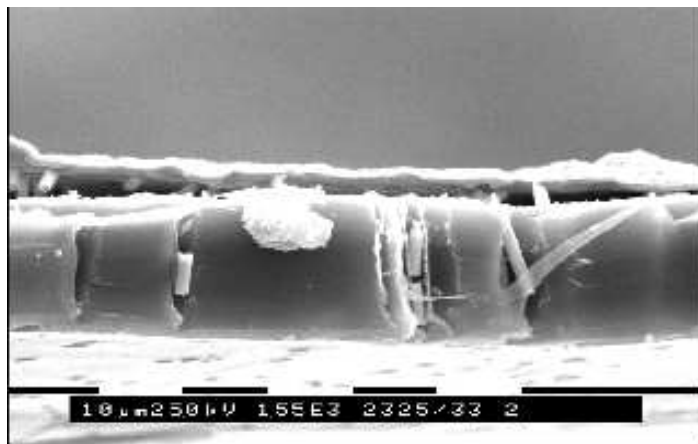


Fig. 3. SEM image of CdS: Mn<sup>2+</sup>: Cu<sup>+</sup> wires - fractured cross section.

SEM images allow the observation of the CdS: Mn<sup>2+</sup>: Cu<sup>+</sup> wires (Fig. 3). Homogeneous 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 that contains in atomic percents: 52.18 S, 36.39 Cd, 7.74 Mn and 3.69 Cu.

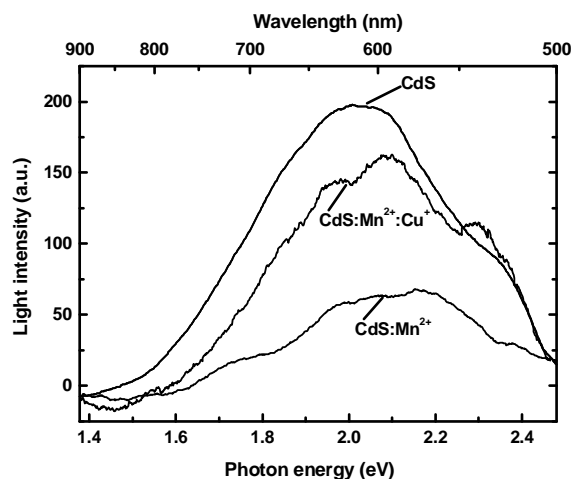


Fig. 4. Emission spectra of the CdS, CdS:Mn<sup>2+</sup> and CdS:Mn<sup>2+</sup>:Cu<sup>+</sup> microwire arrays.

Fig. 4 displays the luminescence spectra of microwires of CdS, CdS:Mn<sup>2+</sup> and CdS:Mn<sup>2+</sup>:Cu<sup>+</sup> created by excitation at  $\lambda = 450$  nm by means of a monochromator. Similar results are obtained for corresponding nanowires. The CdS wires show a broad emission band centered at 620 nm. The intensity of the spectra decreases by manganese doping ( $\sim 7\%$ ), and a new emission peak centered at 580 nm appears. By adding copper the intensity of the 580-nm peak increases and an additional shoulder appears at 680 nm.

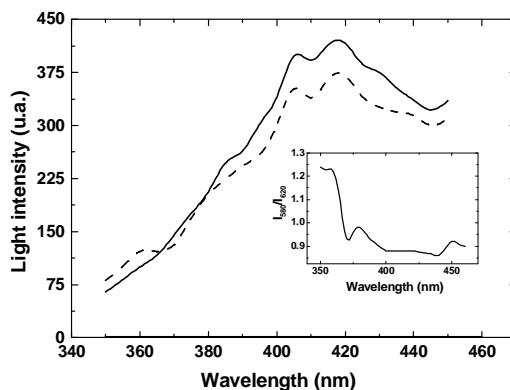


Fig. 5. Excitation spectra of CdS:Mn<sup>2+</sup>:Cu<sup>+</sup> nanowires obtained for the emission bands at 580 (---) and 620 nm (—), respectively (with corrections for wide-band filter, Xe-lamp intensity, and slit width). Inset: Mn<sup>2+</sup> contribution;  $I_{580}$  and  $I_{620}$  being the emission intensities for the two wavelengths.

The excitation spectra with maxima at 580 and 620 nm increase monotonically from 350 to 450 nm (Fig. 5). Their shape is similar due to the partial superposition of the emission centers. The contribution of the centers emitting at 580 nm can be inferred from the ratio  $I_{580}/I_{620}$  vs wavelength (inset Fig. 5), having a specific structure with maxima at 380, 420, and 450 nm.

The comparison of the emission spectra of CdS, CdS:Mn<sup>2+</sup>, CdS:Mn<sup>2+</sup>:Cu<sup>+</sup> allows one to determine the contribution to and the interaction between emitting centers.

### c) CdTe nanowires

CdTe wires were electrodeposited using both acid and basic solutions.

The acid solution contains 300  $\mu$ M TeO<sub>2</sub> and 1 M CdSO<sub>4</sub>, the pH is 1.6 adjusted with H<sub>2</sub>SO<sub>4</sub> and the growth temperature was 80°C.

The solution contains the ions Cd<sup>2+</sup> and HTeO<sub>2</sub><sup>+</sup> and the cathodic reactions for CdTe deposition are:

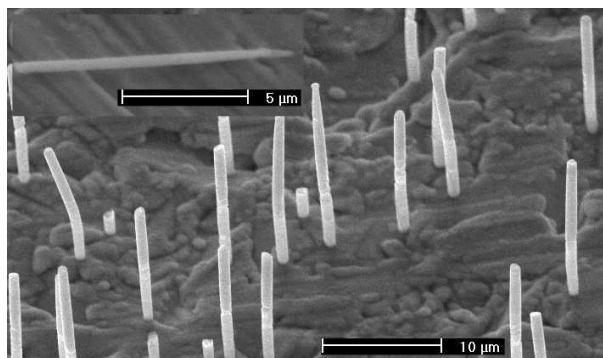
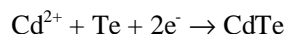
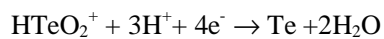
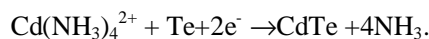
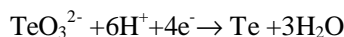


Fig. 6. SEM image of an array of standing CdTe wires 1000 nm diameter prepared by potentiostatic electrodeposition using an acid bath. Inset: fallen nanowire 500 nm diameter.

We deposited CdTe from this acid solution in the membrane nanopores at two different potentials -0.63 and -0.75 V/SCE. A typical morphology of these CdTe nanorods is shown in Fig.6. After the dissolution of the membrane the thicker rods are still standing and their length is equal to the thickness of the foil. The thinner rods were more brittle so during and after the dissolution of the membrane the rods were broken (Fig. 2. inset). We noticed that the nanorods are uniformly distributed on the whole sample area of 1 cm<sup>2</sup>.

The EDX measurements showed in atomic percent, a Cd/Te ratio of 9/1. It is known that the composition of CdTe films depends on the deposition potential. In reference [9] composition studies reveal that deposition in a narrow range of 95 mV, between -0.53 and -0.625 V with respect to a silver-silver chloride (saturated) reference electrode, employing the same solution results in stoichiometric films. Films deposited at more negative potentials have excess Cd and at more positive potentials, excess Te. We assume that the difference in composition for the case of porous membranes when compared to the deposition of films is given by the fact that the volume of the HTeO<sub>2</sub><sup>+</sup> ion is much larger than the Cd<sup>2+</sup> ion. It means that also a large difference in the diffusion coefficients of the two ions inside the pores is expected, this being the reason for the large differences in composition obtained between the deposition of a thin film and of the nanowires.

In another set of experiments, aqueous basic electrolyte containing 50mM CdSO<sub>4</sub>, 10mM Na<sub>2</sub>TeO<sub>3</sub>, 4M NH<sub>3</sub>(aq), 0.5M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (pH=10.7) was used for the electrodeposition of CdTe. In this case the cathode reactions are:



The deposition was performed in membranes with pores diameters in the range 100 – 2000 nm using a potentiostatic regime at -0.8V/SCE.

For the large diameter pores we have noticed a tendency to grow hollow structures instead of rods (figure 7 a). We assume that this can be attributed to the large pores diameter of the used template and, consequently, to a larger deposition current appearing on the pore walls due to a higher value of the electric field.

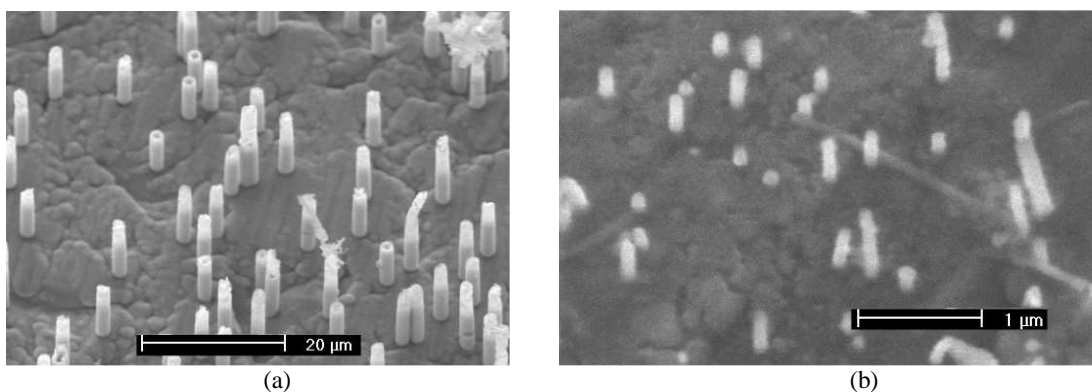


Fig. 7. (a) Array of CdTe hollow structures grown in a membrane with 2 μm diameter pores; (b) 100 nm wires – only short fragments are still standing after membrane removal, fallen fragments can be observed.

For smaller pore dimension the structures grown are not hollow anymore, in figure 7 (b) arrays of wires with diameter 100 nm can be observed. The mechanical stability of these nanorods is low due to the high aspect ratio (especially for the 100 nm ones) and so the nanorods are broken when the polycarbonate membrane is removed.

The EDX measurements revealed a much better stoichiometry when compared to the results obtained by using the acidic bath. For the larger wires the Cd/Te ratio was 1/1.4 while for the thinner ones (800 and 100 nm) in the range 1 ÷ 1.1. This may be due to the fact that the volumes of the two ions: Cd(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup> and TeO<sub>3</sub><sup>2-</sup> are similar which will mean similar diffusion coefficients.

#### 4. Conclusions

Semiconductor nanowires prepared by the template method demonstrate the possibility of fabricating functional structures as photoconductors, temperature detectors or photodiodes.

The next step in our work will be the electrical characterization of such nanowires based on the replication of single pore templates, similar to the characterization of metal nanowires [10]. This will represent an important step in fabricating a new generation of nanowire devices.

The great advantage of the method is the fact that no lithographical techniques and no manipulation of the nanowires will be necessary for electrical characterization. Moreover, the template method in contrast with classical techniques such as electron lithography enables the preparation of such devices in low cost, affordable facilities.

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