

PbSe nanowires grown by the template method

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PbSe nanowires were prepared using the template method. Polycarbonate ion track membranes with pore sizes ranging between 50 nm and 1.5 μm were used as templates. The deposition of PbSe in the pores of the template was performed electrochemically. The influence of the deposition potential and membrane porosity on the morphology and composition of the prepared nanowires was studied. The composition of the wires has been determined by EDX measurements for different potentials. Scanning electron microscopy revealed the morphology of the deposited nanowires. X ray diffraction has been used for structural measurements.

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1. Introduction

New materials with low dimensionality as nanowires or nanotubes, attract an increased focus due to their potential applications in electronics, optoelectronics and in energy conversion devices.

Lead selenide is a narrow bandgap semiconductor ($E=0.28$ eV [1]), being widely used in production of photoresistors, photodetectors and photoemitters for IR region [2-5]. Bulk PbSe is one of the promising materials for the thermoelectric cooling and power generating devices [6].

The electrochemical method allows for obtaining nanostructured semiconductors with the desired electrophysical characteristics (conductivity type, charge carrier concentration). Electrochemical deposition of such semiconductors usually leads to polycrystalline thin films, sometimes even low quality dendritic structures [7,8]. The deposition in confined geometries as is the case for the template method leads to an increase in the structural quality of the material. Low-dimensional structures, such as nanowires offer new ways to manipulate the electron and phonon properties of this material [9].

In previous papers we reported the preparation of nanowires, and alkali halides nanorods [10-12].

In this paper we report the preparation of nanowires and microtubes of PbSe using polycarbonate nanoporous membranes as templates.

2. Experimental

Polycarbonate foils 30 μm thick were irradiated with swift heavy ions (e.g. Au 11.4 MeV/nucleon specific energy). The fluences of the ions were in the range $10^6 - 10^9$ ions/ cm^2 .

Next the samples were sensitized for etching by UV exposure (in order to improve the statistical distribution of geometrical characteristics of the pores obtained after etching). The etching was performed in aqueous NaOH solutions with addition of methanol (5M NaOH, 10%

methanol) at 50°C. The choice of the etching conditions was made according to previous experiments.

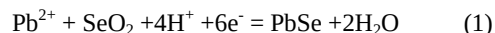
In order to be able to perform the electrochemical deposition, a thin metal film (about 100 nm gold) was sputtered on one face of the membrane; this film was subsequently covered with a thicker layer of copper (a few micrometers) for mechanical stability. Subsequently the membranes were clamped in an electrochemical cell with the pores exposed to the growth solution. The electrochemical deposition of PbSe nanowires was performed with a Voltalab potentiostat controlled by computer and an usual three-electrode cell. A platinum foil and a saturated calomel electrode (SCE) were employed as a counter electrode and reference electrode, respectively. Platinum foil (1 cm^2) and Au/membrane (0.5 cm^2) were used as working electrodes. The electrolyte solution consisted of 1mM SeO_2 , 50 mM $\text{Pb}(\text{NO}_3)_2$ and 0.1 M HNO_3 .

For structural and morphological observations, after the electrodeposition the membrane was dissolved in CH_2Cl_2 . The micro and nanowires were imaged with a Hitachi S-2600N scanning electron microscope while the composition measurements were performed using a EDX (energy dispersive X-ray analysis) device from Rontec GmbH. Structural characterization of the samples was performed by X-ray diffraction using a Shimadzu XRD-6000 diffractometer using CuK_α ($\lambda=1.54056\text{\AA}$) radiation.

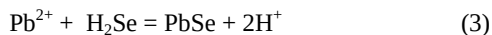
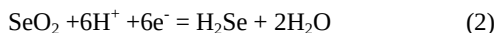
3. Results and discussion

The electrochemical synthesis of lead selenide semiconductor took place in cathodic polarization from electrolyte containing Pb^{2+} and Se^{4+} in presence of nitric acid.

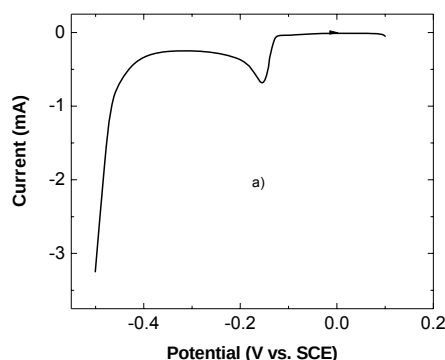
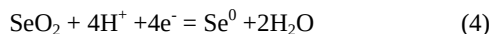
Literature data [7] show the following general process for lead selenide electrodeposition:



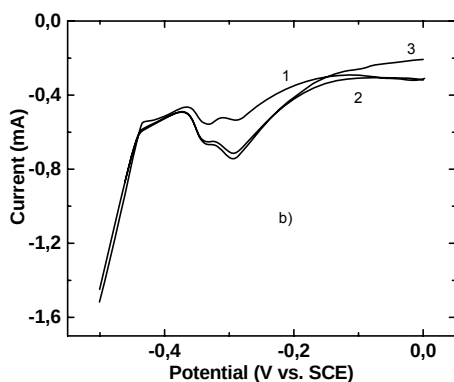
Two different paths are indicated for PbSe electrochemical deposition. The first one considers the initial formation of H_2Se which reacts with Pb^{2+} and is possible when the potential for H_2Se formation is reached:



The second path considers elemental reduction of SeO_2 and Pb^{2+} :



a



b

Fig. 1. a) Cathodic sweep of a platinum electrode and (b) of an Au/polycarbonate membrane (curve 1 first cycle, curve 2 cycle 4 and curve 3 cycle 5) in electrodeposition solution; sweep rate 5 mV/s.

Formation of PbSe phase by cathodic reduction of selenium and lead ions is possible at potentials more positive than Nernst potential E_{Pb^{2+}/Pb^0} due to chemical interaction between overpotentially deposited selenium and underpotentially deposited Pb adatoms [7]. Our

studies followed electrodeposition of PbSe in the conditions of the second path.

Fig. 1 shows the linear voltammetric curves of both platinum electrode and Au/polycarbonate membrane (pore diameter 1.5 μm , 10^7 pores/cm², membrane thickness 30 μm) in electrodeposition solution. The deposition process starts at about -0.12 V vs. SCE for the platinum electrode while for Au/membrane electrode it starts at about -0.16V vs. SCE. One can notice two cathodic peaks on voltammetric curves of Au/membrane electrode (Fig.1,b) in synthesis solution, attributed to different diffusion coefficients of lead and selenium ions into membrane pores. Moreover, for this electrode the deposition peak is cathodically shifted in comparison with the similar peak on voltammogram of platinum electrode. This behavior can be associated with the confinement into the pores, which influences the ion diffusion process towards the electrode.

In the Table 1 are presented the compositions, obtained from EDX measurements, of the PbSe microtube arrays electrodeposited at different potentials. A stoichiometric compound was obtained at potentials around -0.2 V vs. SCE.

Table 1. Atomic percentages as a function of the applied potentials for PbSe microtube arrays.

Potential, V vs. SCE	Pb, at%	Se, at%
-0.345	37	63
-0.3	39	61
-0.2	47	53
-0.16	44	56

We chose to carry out the deposition of PbSe at -0.2V vs.SCE.

The strong current increase, which can be observed in Fig.2 corresponds to the complete filling of the pores, a cap being grown subsequently. This current increase is due to the increase of the deposition surface. By integrating the current in Fig. 2 we can conclude that after the deposition of 11.9 mC, 43.72 mC and 161 mC in membranes containing pores with diameters 1.5 μm , 300 nm and 50 nm, respectively, the pores are completely filled. However a simple calculation shows that the deposited charge is much lower than that needed for filling all the pores in the membrane. Moreover, SEM observations showed that only a fraction of the total number of pores is filled (Fig. 3). We consider these results generated by the strong hydrophobicity of the polycarbonate membrane, some of the pores were not filled with electrolyte thus the growth did not take place. Besides this, other factors affect the degree of pore filling like pore to pore variations in nucleation rate due to adsorbed impurities at the cathode interface; on the other hand, the pores are not identically and if a few pores fill rapidly with PbSe the growth continues laterally across the top surface.

Representative SEM images of PbSe microtubes obtained at different deposition potentials are presented in the Fig. 4. The diameter of prepared PbSe microtubes was 1.5 μm and their length was less than 10 μm .

One can notice that PbSe microtubes deposited at potentials around -0.2V vs. have a superior mechanical strength (few of microtubes are broken).

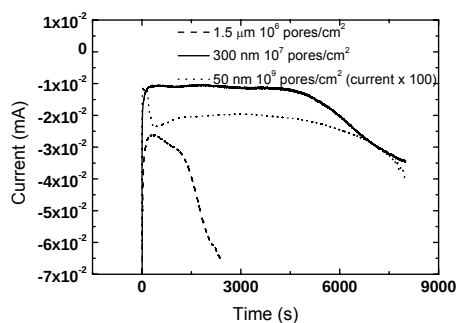


Fig. 2. PbSe deposition at -0.2 V vs. SCE in polycarbonate membranes with different pore diameters and pore densities.

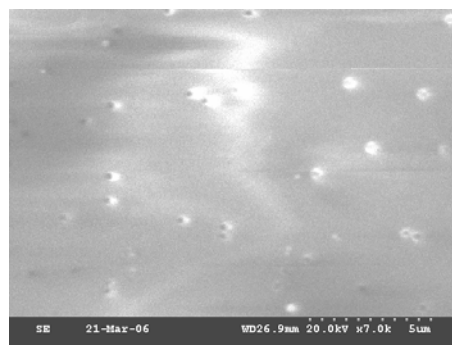


Fig.3. SEM image of a polycarbonate membrane (pore diameter 300 nm, 10^7 pores/cm²) having some pores filled with PbSe tubes.

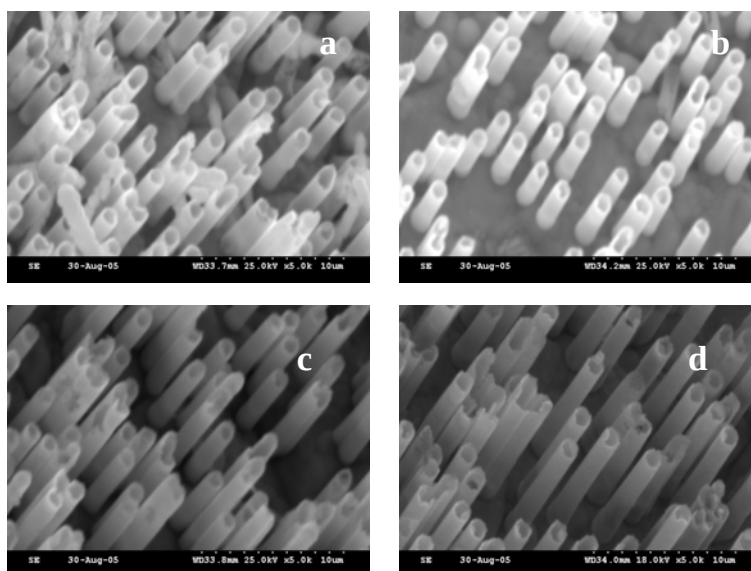


Fig. 4. SEM micrographs of PbSe microtube arrays prepared at (V vs. SCE) a) -0.345, b) -0.3, c) -0.2, d) -0.16.

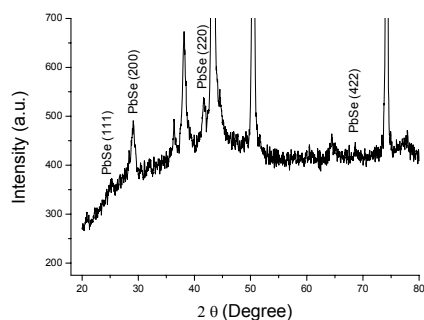


Fig. 5. X-ray diffraction pattern of a PbSe microtubes sample deposited onto CuAu support, at -0.2V vs. SCE.

Synthesis as microtubes hasn't increased the crystalline order of lead selenide. X-ray diffraction pattern of PbSe microtube array, prepared at -0.2V vs. SCE shows (Fig. 5) two dominant peaks, (200) and (220), similar to those of PbSe films electrodeposited at the same potential.

4. Conclusion

PbSe microtube and nanowire arrays were grown using simple electrodeposition method and polycarbonate membranes as template. We observed that the deposition process in polycarbonate membrane is influenced by the limited diffusion of ions into the pores and strong hydrophobicity of membrane. By controlling the

electrochemical parameters it is possible to obtain the stoichiometric compound with the desired morphology. We have found that the electrodeposition at a potential around -0.2V vs. SCE leads to the deposition of polycrystalline microtubes, with a composition close to PbSe.

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