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Semiconductor nanowires obtained by template method

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One-dimensional structures having uniform diameters were prepared by electrochemical deposition using polycarbonate membranes as templates. Lead chalcogenides and ZnO tubes and rods growth processes were presented comparatively. The tendency of PbTe and PbSe semiconductors to grow as tubes both in membrane micro and nanopores was explained based on the absorption of lead ions on the pore wall.

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1. Introduction

Materials such as metals, semiconductors and oxides, exhibit novel electrical, optical and mechanical properties when shaped into nanosized dimensions. One-dimensional vertical nanowires can be fabricated simply by filling up pores in a substrate by means of electrochemical deposition (ECD). The architecture of the porous template or pattern defines the wire shape, direction and size. Because of the extreme aspect ratios of these 3D porous membranes, most physical and chemical vapor deposition techniques are ill suited for this template-directed growth technique. In the case of ECD, the electrolyte solution provides access of reagents deep down in the pores for the deposition process. The ECD is a process which involves charge transfer, diffusion, reaction, adsorption and substrate. Therefore, the structure of nanowires is closely related to deposition conditions and growth modes during the process.

Many fundamental aspects of the ECD of semiconductors are still not known precisely, in particular the deposition mechanism itself. The understanding and control of extrinsic doping, the role of the semiconducting properties of the electrode during the deposition (current transport mechanisms through the semiconductor, charge transfer at the interface, role of back contacts, photoinduced effect) are other examples.

The most important specificity of the electrodeposition of compound semiconductors is in agreement with the Kröger's work [1], where he explained the self regulated composition observed in CdTe films as a consequence of the high free energy of formation of this compound (the formation of the compound instead of elemental layers is favoured by the energy gain in the reaction). Recent works on either chalcogenides (sulfides, selenides, tellurides), oxides or other emerging compounds like thiocyanates, halides confirm the importance and the accuracy of this concept [2].

The deposition potential of lead chalcogenides is determined by less noble component and it is more positive than its reduction potentials. A large excess of the metal precursor M^{2+} is needed in order to make the compound formation reaction more favourable than the reduction of chalcogen X^{4+} on top of itself [3].

Electrodeposition of oxides is different from chalcogenides since oxygen atoms are always present in aqueous solvent and the stable oxidation state of oxygen is 2-. Metal oxide films may be deposited cathodically at potentials more positive than the metals themselves (ZnO [4], Cu_2O [5]) with either NO_3^- or molecular oxygen as the oxygen precursor. The oxide film is usually formed via dehydratation of metal hydroxide. A different approach to the electrodeposition of compounds is electrochemical atomic layer epitaxy (ECALE). In ECALE the compound constituents are deposited from solutions alternately one at the time and the deposition potentials, solution concentrations, pH's etc can be optimized separately [3].

One step epitaxial electrodeposition of semiconductor layers, dots, nanopillars, for chalcogenides, oxides is another example of optimal use of generalized Kröger's concepts. In some cases, like for ZnO, the electrodeposition mechanism can even be considered as an electrochemically induced surface precipitation.

In the present work the growth processes of some lead chalcogenides and ZnO rods and tubes are presented comparatively. Wires composition, morphology and structure were characterized by energy dispersive X ray analysis, scanning electron microscopy and X ray diffraction.

2. Experimental

Commercial polycarbonate (Makrofol N, Bayer Leverkussen) foils irradiated with swift heavy ions are used as template. Before their using, the foils are immersed at 50 ^oC temperature in a 5M NaOH aqueous solution containing 10% in vol methanol in order to etch the ion traks. It followed by deposition on a side of the membrane by sputtering of a thin gold layer, reinforced with a copper layer in an electrochemical process; the metallic part will later play the role of the cathode. In a

subsequent operation, the pores are exposed to an electrolyte solution for growing electrochemically semiconductor micro and nanowires. During electrodeposition in pores a Pt plate was used as auxiliary electrode and a saturated calomel electrode (SCE) was the reference electrode. The electrochemical deposition was accomplished using a Voltalab potentiostat/galvanostat connected to a computer. For subsequent measurements, i.e. electron microscopy and X-ray diffraction the membrane was dissolved in dichlormethane (CH_2Cl_2). The micro and nanowires were imaged using a Hitachi S-2600N Scanning Electron Microscope having for composition measurements an EDX (energy dispersive X-ray analysis) device from Röntec GmbH. The X-ray diffraction spectra (XRD) of the samples were recorded with a Shimadzu XRD-6000 diffractometer using CuK_α (λ=1.54056Å) radiation.

3. Results and discussion

In general, pure, crystalline, nanosized semiconductor with a narrow size distribution is highly desirable to serve most of their intended purposes, especially in the rapidly developing nanoelectronic and nanooptoelectronic devices. The combination of the large band gap and exciton binding energy has generated excitement for the development of ZnO ultra-violet (LTV) detectors, blue light emitting diodes, and blue lasers. On the other hand, the transport properties of these 1D systems are very different from bulk similar materials; the thermoelectric properties of PbTe and PbSe nanowires can be improved in comparison with the bulk lead chalcogenides.

a) PbTe and PbSe nano and microtubes

PbTe and PbSe semiconductor compounds were electrodeposited using acid solutions [5, 6], containing 100 mM HNO_3, 1mM TeO_2, 50mM $Pb(NO_3)_2$, and, respectively 100 mM HNO_3, 1mM SeO_2, 50 mM $Pb(NO_3)_2$,. We deposited PbTe and PbSe compounds from acid solutions in the membrane pores at potential –0.345 and -0.2V/SCE, respectively (Fig.1). A typical morphology of PbTe and PbSe nano and microtubes is shown in the SEM images from Fig. 2.

We observe the tendency of PbTe and PbSe semiconductors to grow as tubes both in membrane micro and nanopores.

Adsorption is a method for removing lead from wastewater. A study [6] on the adsorption mechanism of an adsorbent based on natural condensed tannin indicated that it operated in aqueous solutions as an ionic exchanger whose end group was sodium ion (Na^+). One lead (II) ion (Pb^{2+}) was adsorbed onto the adsorbent by taking the place of two Na^+ ions. The pH influenced the extraction of lead from aqueous solutions, the adsorbent offering favorable characteristics in lead removal in acid solutions. We consider our polycarbonate membrane treated in NaOH solution similar with this natural adsorbent. In nano and micropores, on polymer surface, lead islands will appear when the polycarbonate membrane is immersed in PbTe or PbSe deposition solutions. Due low solubility of the PbX compound, a thin layer can be formed on the polymer surface; this material will orientate the electrochemical growth of PbTe and PbSe on the pore wall and a micro or nanotube will be obtained.

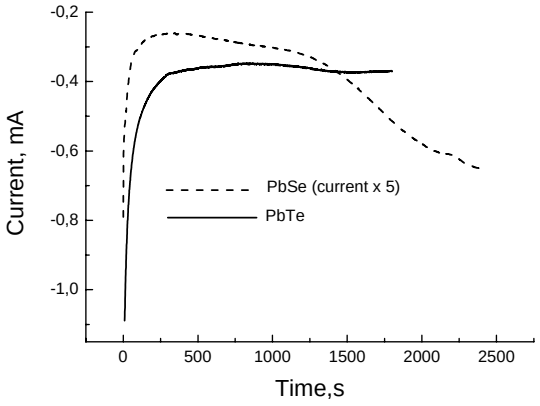


Fig. 1. PbTe (——) and PbSe (-----)deposition into the pores of polycarbonate membranes (pores diameter – 1.5μm, pores density – 10^6 /cm^2, membrane surface area – 1 cm^2) at potentials of –0.345 and -0.2 V/SCE, respectively.

The PbTe and PbSe microtubes compositions are (at%): Pb 53.1, Te 46.9 and Pb 46.54, Se 53.43, respectively

b) ZnO wires

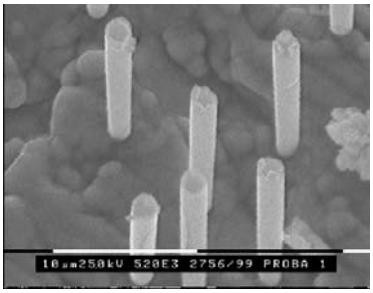
ZnO wires were prepared by electrodeposition from a solution containing 0.05M $Zn(NO_3)_2$ at a potential of -0.7V/SCE; the temperature of solution was 70 ^oC.

An important step in electrochemical process of ZnO formation is the reduction of nitrate ions and the increase of local pH with $Zn(OH)_2$ precipitation. The hydroxide is subsequently dehydrated and converted to ZnO in the hot solution (70^0C). The deposition potential and the cathodic material controlle the nucleation and growth process of ZnO wires [7].

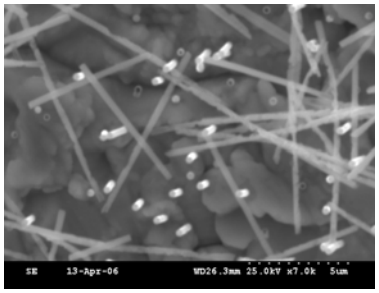
It was observed (Fig.3) that the cathodic current decreases quickly at initial time and increases gradually for a short time (this increase is pronounced for growth of the wires in large pores, 1.5μm). The initial decrease of the current is attributed to formation of ZnO nucleus and gradual increase corresponds to growth of ZnO wires. The following step (a current decrease) is the result of ions diffusion through the pores; finally, the current increases again due to the growth of ZnO compound outside of the pore.

ZnO grew preponderantly like a rod (Fig.4), the origin of this behavior is the existence of the $Zn(OH)_2$ precipitation step in the synthesis process.

The diffraction spectrum (Fig. 5) shows the growth of ZnO wire as a stoichiometric compound.



a



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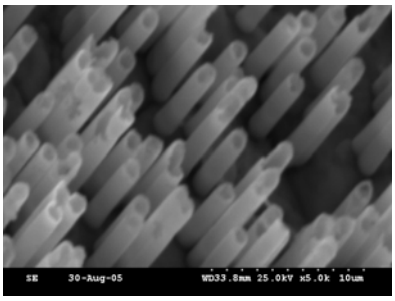
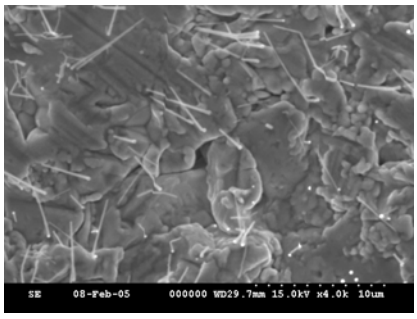


c



d

Fig.2. PbTe (a and b) and PbSe (c and d) micro (diameter ~ 1.5 µm) and nanotubes (diameter ~ 300 nm) obtained in polycarbonate membranes.

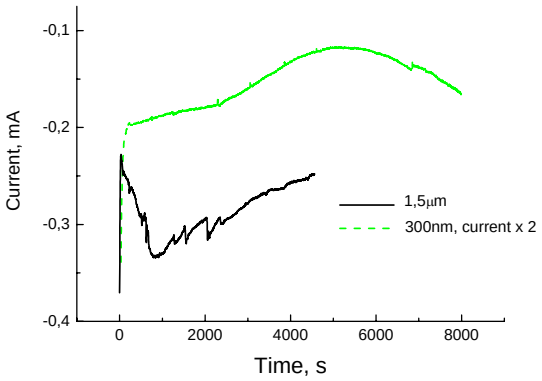


Fig. 3. Chronoamperometric curves registered during the deposition of ZnO wires from 0.1M $Zn(NO_3)_2$ solution, at 70℃ in: (-----) membrane with 10^7 pores/cm^2, 300nm diameter and (——) membrane with $5x10^6$ pores/cm^2, 1.5µm diameter; the deposition potential: -0.7V/SCE and the electrode surface area: 1cm^2.

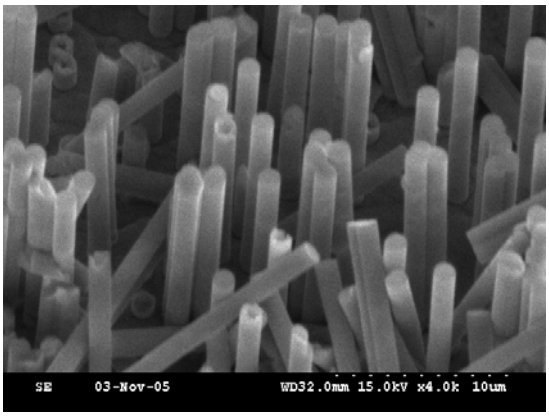


Fig. 4. ZnO rods and tubes (diameter~1.5 µm) obtained in polycarbonate membranes.

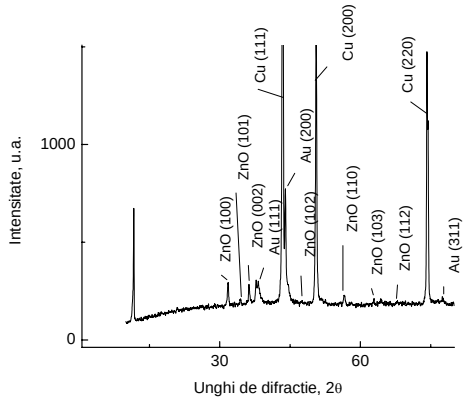


Fig. 5. Diffraction spectrum of ZnO microwires supported by a Cu/Au foil.

4. Conclusions

ZnO wires and PbTe and PbSe micro and nanotubes were prepared by electrochemical deposition using polycarbonate templates.

Growth of PbTe and PbSe as tubes was explained on the basis of lead adsorption on NaOH treated polycarbonate membrane; islands of thin film of PbX will appear on pore wall. This material will orientate the electrochemical growth of PbTe and PbSe on the pore wall and a micro or nanotube will be obtained.

ZnO will grow like a rod due to the precipitation step in synthesis process and, as a consequence, the growth process of ZnO wires is slowly compared to growth of PbTe and PbSe tubes.

References

[1] F. A. Kröger, J. Electrochem. Soc. **125**, 2028 (1978).
[2] D. Lincot, Tin Solid Films, **487**, 40 (2005).
[3] H. Saloniemi, Doctoral thesis: Electrodeposition of PbS, Pbse and PbTe thin films, University of Helsinki, 2000, http://virtual.vtt.fi/inf/pdf/publications/2000/p423.pdf
[4] S. Peulon, D. Lincot, Adv.Mater. 8(1996) 166
[5] E. W. Bohannan, M. G. Shumsky, J. A. Switzer, Chem. Mater. **11**, 2289 (1999).
[6] Xin-Min Zhan, X. Zhao, Water Research **37**, 3905 (2003).
[7] B. Cao, W.Cai, H. Zeng, G. Duan, J. Appl. Phys. **99**, 073516-1 (2006).

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