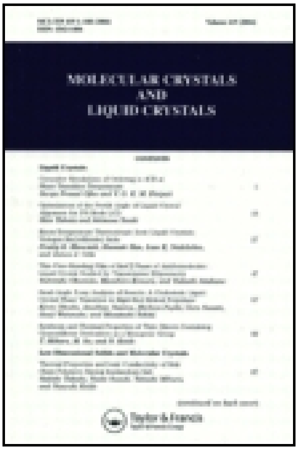

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Electrochemical Deposition of PbSe1-xTex Nanorod Arrays Using Ion Track Etched Membranes as Template

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ELECTROCHEMICAL DEPOSITION OF $PbSe_{1-X}Te_X$ NANOROD ARRAYS USING ION TRACK ETCHED MEMBRANES AS TEMPLATE

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Lead chalcogenides (PbS, PbSe, PbTe) are narrow band gap semiconductors which have been studied in the field of IR detection and thermoelectric devices. The template method is a general approach for synthesizing nanomaterials within the pores of membranes. The membranes employed contain cylindrical pores with monodisperse diameters, and corresponding cylindrical nanostructures are obtained. The aim of the present study was to prepare $PbSe_{1-x}Te_x$ *nanorod arrays using electrodeposition. The process was investigated by cyclic voltammetry and electrochemical impedance spectroscopy. The resulted* $PbSe_{1-x}Te_x$ *nanostructures were characterized using scanning electron microscopy (SEM) as well as energy dispersive X-ray analysis (EDAX).*

Keywords: electrodeposition; ion track membranes; nanorods; PbSeTe semiconductor

INTRODUCTION

Preparation of nanowires and nanowire based devices has attracted more and more interest in the last period of time. One of the most convenient method to prepare such quasi 1-D structures is the template replication. It consists in filling the pores of a membrane (most often ion track membranes or anodic alumina) with the desired material, usually by electrodeposition.

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A class of materials suited for this approach are compound semiconductors such as II–VI or IV–VI group. The reason for increasing interest of preparation of semiconductor nanowire or nanowire devices is the wide field of applications, from different types of sensors to light emitting diodes [1–3].

$PbSe_{1\text{-}x}Te_x$ is a well known thermoelectric material; recently, the topic of size effects of the thermoelectric materials has become important in thermoelectricity because there have been reported enhancements of the dimensionless figure of merit, ZT, for low dimensional structures [4]. On the other hand, according to scaling factors, the attractive idea in the manufacturing of a thermoelectric microdevice is to increase specific power (W/cm^2) by reducing the size of the thermoelectric elements, while maintaining the same aspect ratio of the elements as in larger thermoelectric devices.

We describe here the preparation of $PbSe_{1\text{-}x}Te_x$ nanorod arrays by potentiostatic electrodeposition using a polycarbonate track etch membrane as template.

EXPERIMENTAL

Polycarbonate (Makrofol N, Bayer Leverkussen) ion track membranes with $\sim 30\,\mu m$ thickness and pore densities of 10^6 and $10^8\,cm^{-2}$ were used as templates for electrodeposition of $PbSe_{1\text{-}x}Te_x$. For the experiments described we used membranes with pores of 100–2000 nm diameter. First, a copper film, which will play later the role of cathode, was chemically deposited on one side of the membrane; this film was reinforced by further electrochemical plating of copper. The potentiostatic deposition of $PbSe_{1\text{-}x}Te_x$ semiconductor and impedance spectroscopy measurements were accomplished with a Zahner Electrik, Model IM6 apparatus connected to a PC. As reference electrode a commercial saturated calomel electrode (SCE) and as auxilliar electrode a platinum mesh were used. In an additional experiment the working electrode was a Pt wire ($0.065\,cm^2$). After the electrodeposition process the polymer membrane was dissolved in CH_2Cl_2. The nanostructures were imaged by scaning electron microscopy, whereas the composition of semiconductor was determined by energy dispersive X-ray analysis (EDAX).

RESULTS AND DISCUSSION

$PbSe_{1\text{-}x}Te_x$ compound semiconductor was electrodeposited using an acid solution [5,6], containing 0.1 M HNO_3, 0.05 M $Pb(NO_3)_2$, 0.001 M H_2SeO_3 and 0.0006 M TeO_2. In Figure 1 are presented comparatively the cyclic

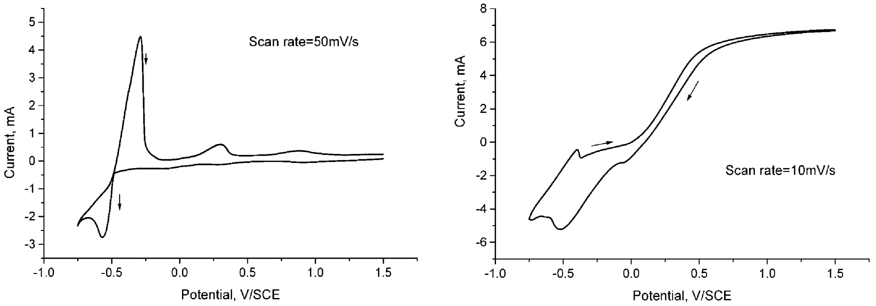


FIGURE 1 Cyclic voltammograms of platinum electrode ($S = 0.065\,cm^2$) (*left side*) and copper/membrane electrode ($S = 0.8\ cm^2$) (*right side*) in the solution containing 0.1 M HNO_3, 0.05 M $Pb(NO_3)_2$, 0.001 M H_2SeO_3 and 0.0006 M TeO_2; the diameter of membrane pores was 100 nm and pores density $10^8\,cm^{-2}$.

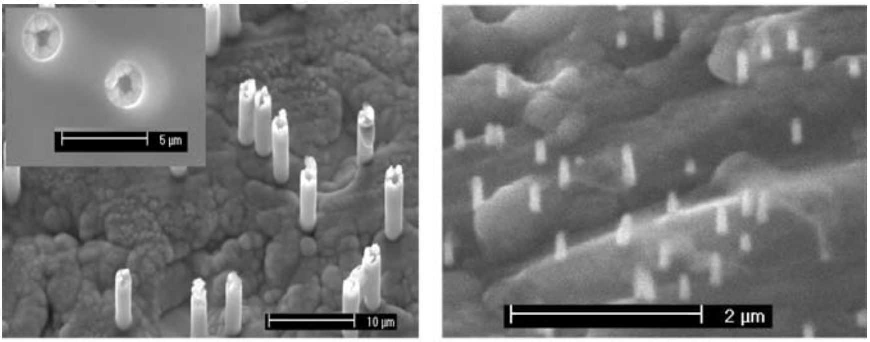
voltammograms of both Pt and copper/membrane electrodes in the synthesis solution. We noticed that the process of Pb, Se, Te ternary codeposition from the above solution starts at -0.1 V and shows a maximum current at -0.5 V/SCE. The presence of Pb, Se, Te elements in the corresponding deposit is proved by voltammetric maxima at -0.3, 0.3 and 0.9 V/SCE, respectively, on the anodic branch. Using a copper/membrane electrode as working electrode a similar process in the same potentials range was evidenced (Fig. 1). Moreover, on this cyclovoltammogram appears the anodic behavior (the dissolution, mainly) of copper electrode deposited on one side of polycarbonate membrane.

The micrographs showing the morphology of $PbSe_{1\text{-}x}Te_x$ microtubes and nanorods are presented in Figure 2. The composition of $PbSe_{1\text{-}x}Te_x$ nanostructures was determined by EDAX technique and it is expressed by $x = 0.37$ for $PbSe_{1\text{-}x}Te_x$ compound prepared at -0.337 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.

This different behavior *versus* membrane pores diameter is also observed by interpreting the electrochemical impedance spectra of copper/membrane electrodes. Nyquist and Bode impedance spectra of copper/membrane electrodes with two kinds of pores at equilibrium potential (-0.025 V) in solution containing 0.1 M HNO_3, 0.05 M $Pb(NO_3)_2$, 0.001 M H_2SeO_3 and 0.0006 M TeO_2 are presented in the Figures 3 and 4.

We have chosen from literature [7] the equivalent circuit (EQC) scheme for a metal coated with a porous film. This circuit is shown in Figure 5, where R_m and C_m are the resistance of electrolyte in pores and capacitance



(a) (b)

FIGURE 2 SEM images of $PbSe_{1-x}Te_x$ microtubes and nanowires prepared by potentiostatic electrodeposition in ion track membranes at -0.337 V/SCE: (a) microtubes deposited in 2000 nm diameter pores; (b) nanowires deposited in 100 nm diameter pores.

of polycarbonate membrane, R_p, C_{dl} are resistance and capacitance of metal/electrolyte interface, respectively and Z_w is Warburg impedance. We also denoted by R_e–the electrolyte resistance.

As can be seen, the Bode plot from Figure 3 shows only a time constant and a resistive behavior of the copper/membrane electrode. A ZARC-Cole distributed element [8] representing a constant phase element, *cpe*, in parallel with a resistor, as illustrated in Figure 6a, was used to describe such electrode behavior, when pores diameter of the membrane is about 2000 nm. Usually, *cpe* is considered to be the intrinsic equivalent of an

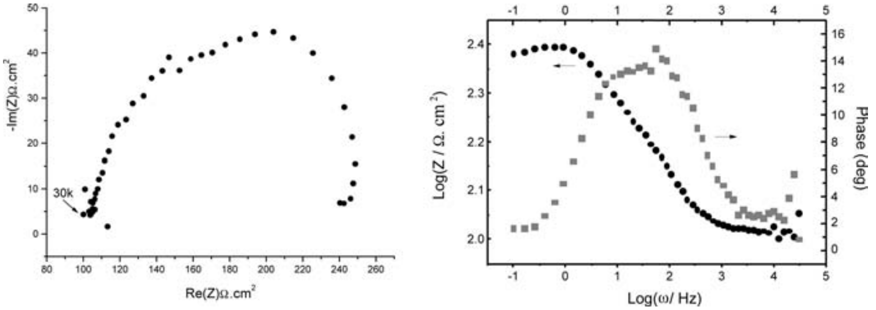


FIGURE 3 The electrochemical impedance spectra of copper/membrane electrode (pores diameter 2000 nm) at equilibrium potential in solution containing 0.1 M HNO_3, 0.05 M $Pb(NO_3)_2$, 0.001 M H_2SeO_3 and 0.0006 M TeO_2; *left side* – Nyquist plot; *right side* – Bode plot.

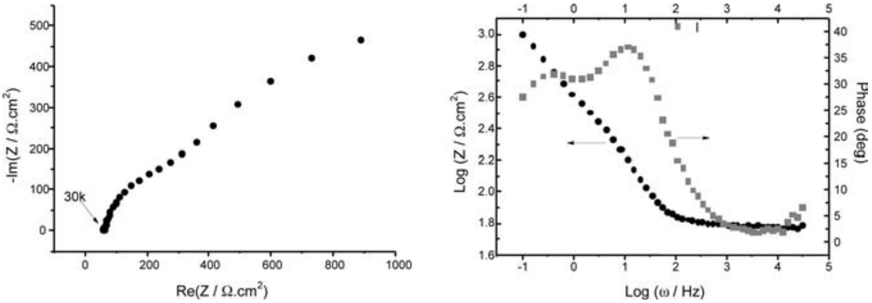


FIGURE 4 The electrochemical impedance spectra of copper/membrane electrode (pores diameter 100 nm) at equilibrium potential in solution containing 0.1 M HNO_3, 0.05 M $Pb(NO_3)_2$, 0.001 M H_2SeO_3 and 0.0006 M TeO_2; *left side* – Nyquist plot; *right side* – Bode plot.

interfacial capacitance and R_p is the resistive component of the irreversible charge transfer process at the electrode. On the other hand, the *cpe* element takes into account the displacements of the ions in porous electrode. The mathematically equivalent expression for the response of this distributed element may be written as

$$Z = R/[1 + (i\omega\tau)^{\Psi}],$$

where τ is a relaxation time and Ψ is a parameter that accounts for the distribution of τ around a mean value τ_0.

Table 1 presents the values of the circuit elements shown in the Figure 6.

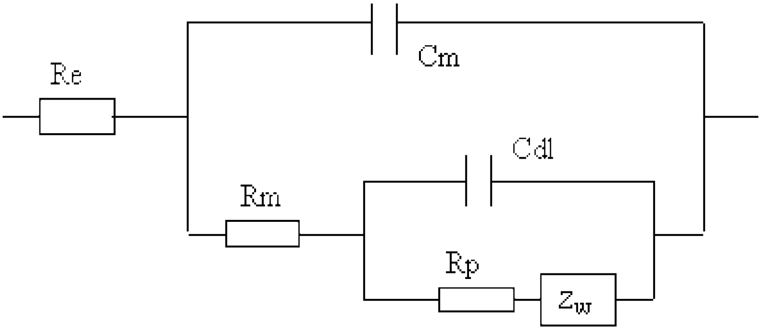


FIGURE 5 The equivalent circuit [7] for a metal coated with a porous film. The meaning of symbols: R_m, C_m – the resistance of electrolyte in pores and capacitance of porous membrane, R_p, C_{dl} – resistance and capacitance of metal/electrolyte interface, Z_w – Warburg impedance, R_e – the electrolyte resistance.

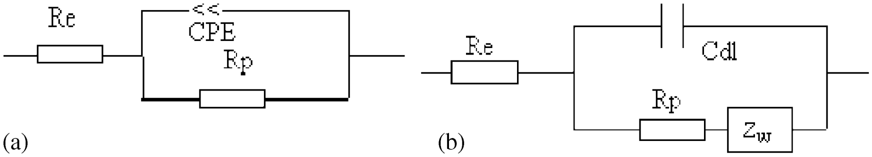


FIGURE 6 The proposed equivalent circuits for copper/membrane electrode with large pores (2000 nm diameter) (Fig. 6a) and with small pores (100 nm diameter) (Fig. 6b), respectively, in solution containing 0.1 M HNO_3, 0.05 M $Pb(NO_3)_2$, 0.001 M H_2SeO_3 and 0.0006 M TeO_2.

TABLE 1 The Parameters of the Equivalent Electric Circuits (EQCs) (shown in Figure 6) for Copper/Membrane Electrode with Large Pores (2000 nm diameter) and with Small Pores (100 nm diameter) in Solution Containing 0.1 M HNO_3, 0.05 M $Pb(NO_3)_2$, 0.001 M H_2SeO_3 and 0.0006 M TeO_2

Electrical parameter	EQC from Figure 6a	EQC from Figure 6b
R_p/Ω	16.6	10^{-8}
$C_{dl}/\mu F$	–	$4{\cdot}10^{-5}$
τ	$3.83{\cdot}10^{-4}$	4.788
Ψ	0.6	0.4
Z_W/Ω	–	1411

The obtained data for the copper/membrane electrode with diameter of membrane pores of 100 nm (Fig. 4) are fitted with an equivalent circuit scheme presented in the Figure 6b. In this case, the Bode diagram (Fig. 4) shows beside the impedance of the metal/electrolyte interface an impedance part due to mass transport process into membrane pores. To express this impedance in equivalent circuit we used a generalized finite Warburg (GFW) distributed element [8]. The mathematical expression for this element response is:

$$Z_{GFW} = R \tanh\left([i\tau\omega]^{\Psi}\right)/(i\tau\omega)^{\Psi},$$

where τ is here the dielectric constant, Ψ has the value in the range $0 < \Psi < 1$ and R a diffusion resistance. One can observe from Table 1 the great contribution of diffusion at electrode impedance.

CONCLUSIONS

We prepared nanorod and microtube arrays of $PbSe_{1\text{-}x}Te_x$ using potentiostatic deposition in the pores of a polycarbonate track etch membrane, from nitric acid solution. SEM measurements have shown the growth by electrodeposition of uniform nanostructure arrays on large surface areas. EDAX measurements showed a composition expressed by $x = 0.37$ for $PbSe_{1\text{-}x}Te_x$ nanostructures prepared at -0.337 V/SCE.

The pores diameter controls the electrochemical growth of $PbSe_{1\text{-}x}Te_x$ semiconductor as rods (in membranes with small pores) or tubes (in the case of larger pores). Impedance measurements confirmed this different behavior of copper/membrane electrode having small and, respectively, large pores.

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