

PbSe_{1-x}Te_x THICK THERMOELECTRIC FILMS OBTAINED BY ELECTROCHEMICAL DEPOSITION FROM AQUEOUS SOLUTIONS

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It is presented a study of PbSe_{1-x}Te_x thick films electrodeposition on glassy carbon and ITO electrodes in acid solutions (0.1M HNO₃), using cyclic voltammetry and rotating-disk techniques. Electrochemical impedance spectroscopy study of PbSe_{1-x}Te_x film in 0.1M HNO₃ is reported.

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1. Introduction

Lead chalcogenides (PbS, PbSe, PbTe) are narrow band gap semiconductors which have been studied in the field of IR detection and thermoelectricity.

The bandgap energy of these compounds can be tailored to cover some regions of the IR spectrum by adjusting alloy composition. Lead chalcogenides films were been prepared by epitaxy [1-3], chemical deposition [4-5], and electrochemical deposition [6-8].

Electrodeposition can be carried out using substrates with different size and shape. The reactions involved occur closer to the equilibrium potential and the deposition process can be controlled easier than in many high temperature gas phase methods. In addition, toxic gaseous precursors do not have to be used unlike in chemical gas phase methods. In the semiconductors electrodeposition process it is important to obtain a polycrystalline, stoichiometric material, with large crystallites. Although the semiconductor electrodeposition is similar to metallic alloys electrodeposition [9], some problems appear due to the large differences between reduction standard potentials (E^0) of selenium, tellurium ions and those potentials for the most part of metals. This changes the deposition nature during electrodeposition due to the presence of the metastable states and the semiconductor nature of deposited film.

In this work, voltammograms of pure or mixture compounds of Pb(NO₃)₂, TeO₂, SeO₂, PbSe, PbSe_{1-x}Te_x were recorded in order to understand electrochemical deposition and dissolution processes of PbSe_{1-x}Te_x. A study of electrochemical impedance spectroscopy on PbSe_{1-x}Te_x dissolution is also presented.

2. Experimental

The acid solutions (0.1M HNO₃) used in electrochemical deposition of the lead, selenium, tellurium and theirs compounds, PbSe, PbSe_{1-x}Te_x contained dissolved 0.05M Pb(NO₃)₂, 0.01M H₂SeO₃, 0.01M TeO₂, 0.05M Pb(NO₃)₂+0.001M H₂SeO₃, 0.05M Pb(NO₃)₂+0.001M H₂SeO₃+0.0006M TeO₂. We have used a three-electrode electrochemical cell without anodic and cathodic space separation. The reference electrode was a saturated calomel electrode (SCE) and the auxiliary electrode was a platinum sieve; as working electrodes we used a glassy carbon rotating disk ($S=0.125\text{ cm}^2$) and ITO (0.5 cm^2) electrodes.

The voltammetric curves were recorded at room temperature using a potentiostat/galvanostat PAR 173 coupled with a computer. The impedance measurements were achieved on a TFA-2000A, AC Impedance Analyzer made by Sycopel Scientific.

3. Results and discussion

According with the general chemical reaction for cathodic deposition, the deposition of semiconductors can be written in a generalized form as:



Fig. 1. Rotating disk polarization curves (glassy carbon) for reduction of lead (1), selenium (2) and tellurium (3) ions from acid solutions (0.1M HNO₃) containing dissolved 0.05M Pb(NO₃)₂, 0.01M H₂SeO₃, and 0.01M TeO₂, respectively; rotation rate = 500 rpm; sweep rate = 0.5 mV/s.

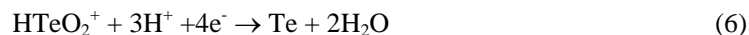
The polarization curves for reduction of lead, selenium and tellurium ions from acid solutions (0.1M HNO₃) containing dissolved 0.05M Pb(NO₃)₂, 0.01M H₂SeO₃, and 0.01M TeO₂, respectively, are presented in Fig.1. The lead starts to deposit on glassy carbon surface at -0.2V/SCE, with a maximum at about -0.28 V/SCE, according to equation (4):



The deposition of selenium starts at a potential of -0.23V/SCE, with a maximum at about -0.55V/SCE and can be represented by equation:



The acid solution for tellurium electrodeposition contains HTeO₂⁺ ions. The reduction process involves the transfer of four electrons:



The reduction takes place at a potential of about -0.33 V/SCE. The two stages for the deposition of Se films on glassy carbon electrode can be explained by catalytic behavior of carbon surface. Our similar studies carried out on ITO electrodes reveal just a single stage in deposition of Se and Te films. The electrochemical deposition and dissolution processes of lead, selenium and tellurium were also studied by cyclic voltammetry (Fig.2). Our measurements indicated that lead, selenium and tellurium deposited on glassy carbon rotating disk start to dissolve at potentials of +0.023, +0.09 and +0.47 V/SCE, respectively. The lead deposition on tellurium surface takes place at higher current densities compared with the deposition process on carbon surface.

On the other hand, the cyclic voltammogram of glassy carbon rotating disk electrode in acid solution (0.1M HNO₃+0.01M H₂SeO₃) reveals the presence of two oxidation and two reduction potentials. Both the tellurium and selenium voltammograms show the presence of a hysteresis in the region of deposition potentials, indicating that their reduction occurs easier on tellurium and selenium, respectively.

The electrochemical deposition of PbSe (Fig. 3, a) was carried out on glassy carbon rotating disk electrode covered with a selenium layer, to prevent a bad deposition of this compound on carbon substrate. The deposition process starts at -0.16V/SCE, probably with lead electrodeposition on Se surface. This electrode surface induces an anodic shift of the deposition potential.

The sweeping towards negative potentials produces a new electrode surface where the deposition process goes on with difficulty (Fig. 3). Using an approach [10] based on induced codeposition of Se, we consider that the electrodeposition of PbSe can occur at -0.32 V/SCE. The oxidation process of the compound starts at -0.008V/SCE; the cyclic voltammogram shows a wide hump with a maximum at +0.25 V/SCE for this process.

Fig. 3b shows the cyclic voltammogram of glassy carbon rotating disk electrode in acid solution 0.1M HNO₃ + 0.05M Pb(NO₃)₂+0.001M H₂SeO₃+0.0006M TeO₂. The cyclic voltammogram is similar to that of PbSe electrodeposition. Additionally, we observe a small peak attributed to the anodic dissolution of tellurium, at +0.5 V/SCE.

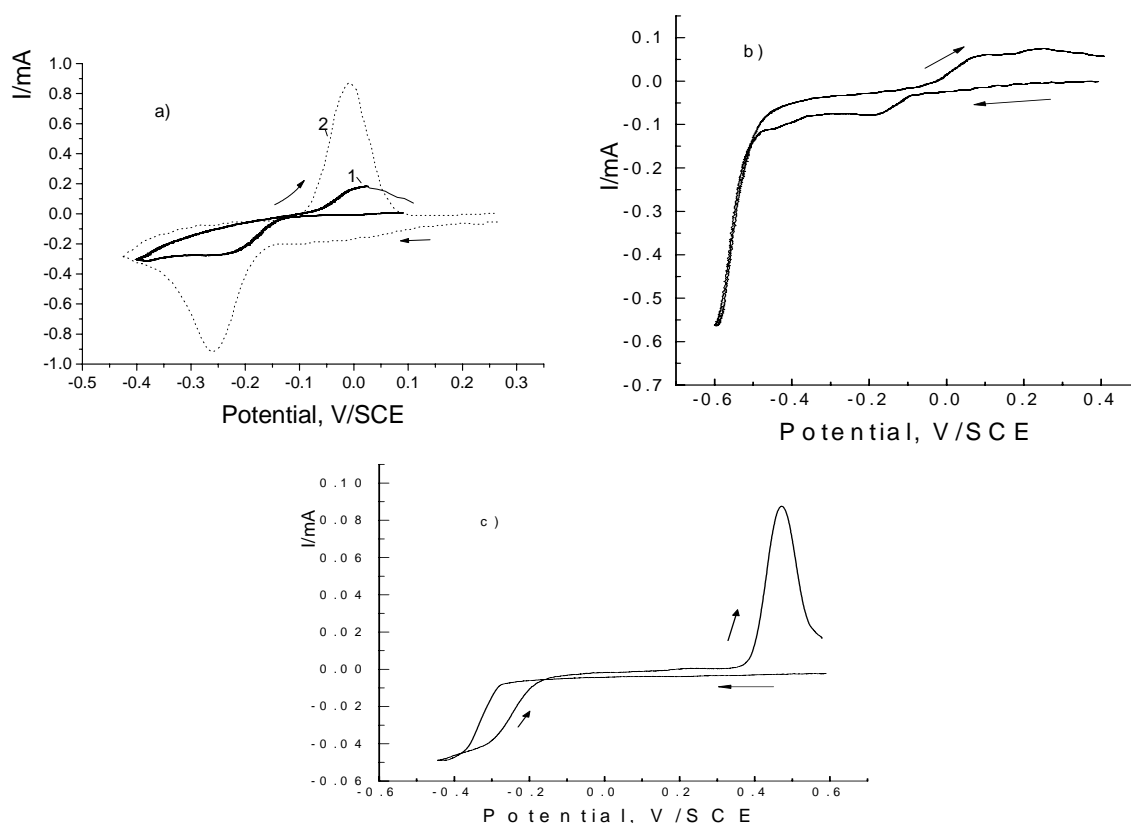


Fig. 2. Cyclic voltammograms of glassy carbon rotating disk electrode in acid solution (0.1M HNO₃) containing: a) 0.05M Pb(NO₃)₂ (curve 1; for the curve 2 the carbon electrode was initially covered with Te); b) 0.01 M H₂SeO₃; c) 0.01 M TeO₂; sweeping rate = 20 mV/s; rotation rate=500 rpm.

From analysis of cyclic voltammograms and polarization curves we are led to the conclusion that the electrochemical deposition of PbSe_{1-x}Te_x compound takes place at a potential around -0.39 V/SCE. The same studies were made on ITO electrode with the results. In the case of a solution ten times more concentrated we notice an important anodic shift of deposition and dissolution potentials (Fig. 4).

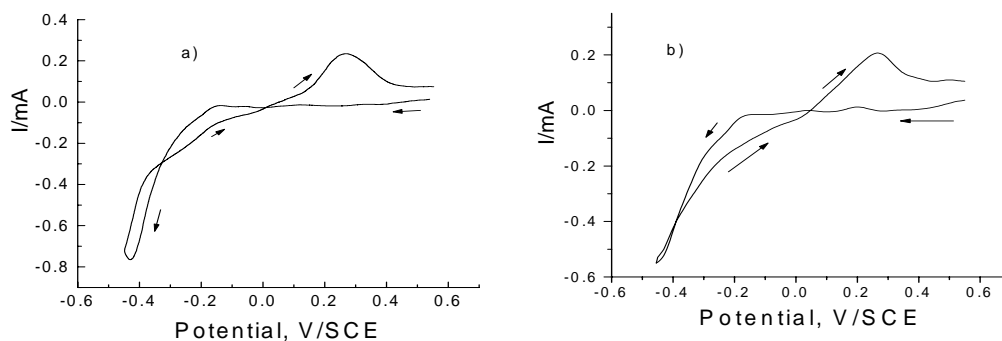


Fig. 3. Cyclic voltammograms of glassy carbon rotating disk electrode in acid solution 0.1M HNO_3 + 0.05M $\text{Pb}(\text{NO}_3)_2$ + 0.001M H_2SeO_3 (a), and 0.1M HNO_3 + 0.05M $\text{Pb}(\text{NO}_3)_2$ + 0.001M H_2SeO_3 + 0.0006M TeO_2 (b); sweep rate=20 mV/s; rotation rate=500 rpm

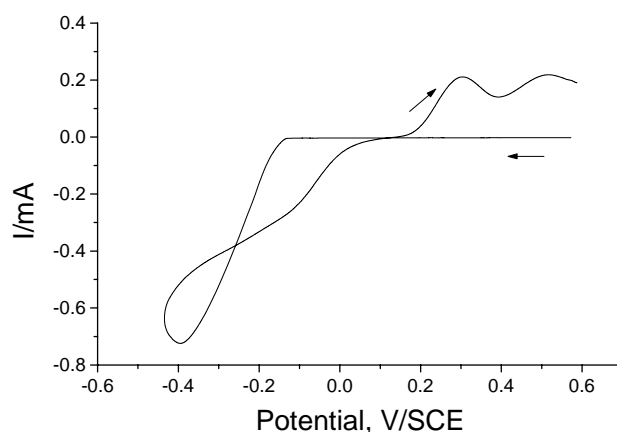


Fig. 4. Cyclic voltammograms of ITO electrode in acid solution 0.1M HNO_3 + 0.05M $\text{Pb}(\text{NO}_3)_2$ + 0.001M H_2SeO_3 + 0.0006M TeO_2 ; sweep rate=20 mV/s.

The impedance spectra of $\text{PbSe}_{1-x}\text{Te}_x$ semiconductor electrochemically prepared on ITO electrode are presented in Fig.5. The Bode diagrams for the ITO/ $\text{PbSe}_{1-x}\text{Te}_x$ show a resistive region on a wide frequency spectrum and a diffusional region at low frequencies.

The general shape of Bode diagrams (Fig.5.b,c) curves do not change when the applied anodic potential increase, but the impedance of the cell reduces. The Nyquist diagram (Fig.5.a) shows two time constants in series with the solution resistance, according to the voltammetric data, which indicate the start of the anodic oxidation process at 0.0 V/SCE.

The diffusional component can be attributed to the Pb and Se ions crossing through incipient oxide layer. The resistive part is attributed to the $\text{PbSe}_{1-x}\text{Te}_x$ and oxide layers.

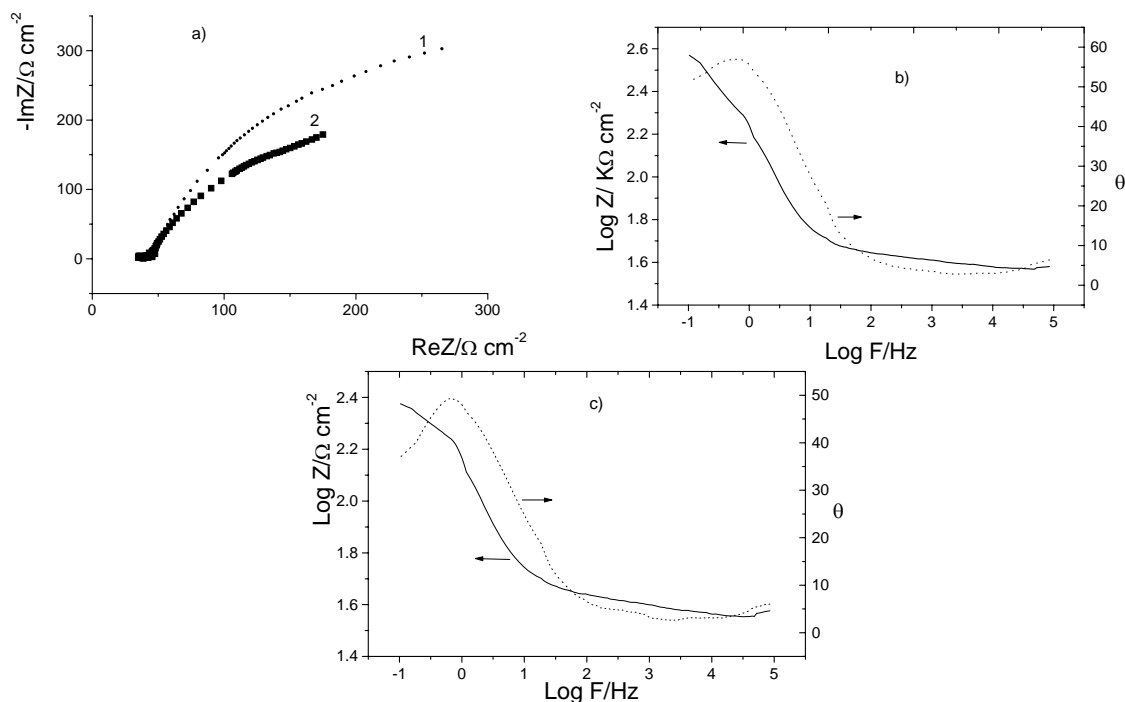


Fig. 5. a) Nyquist diagram for the ITO/PbSe_{1-x}Te_x electrode in 0.1M HNO₃ at: 1) 0.0V/SCE; 2) 0.1V/SCE. Bode diagrams for the ITO/PbSe_{1-x}Te_x electrode in 0.1M HNO₃ at: b) 0.0V/SCE; c) 0.1V/SCE

4. Conclusions

We have presented the voltametric and impedance measurements taken during the PbSe and PbSe_{1-x}Te_x deposition and dissolution. These measurements allowed us to determine the deposition potentials of PbSe and PbSe_{1-x}Te_x compounds and the influence of the electrode substrate on potential deposition. The results indicate that the electrodeposition of PbSe_{1-x}Te_x occurs at 0.39-0.4 V/SCE both at glassy carbon and ITO electrodes.

A scheme of dissolution process of PbSe_{1-x}Te_x film was proposed from electrochemical impedance spectroscopy data.

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