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Electrochemical approaches for rearrangement of lead sulfide thin films prepared by SILAR method

Ümit Çağrı Üst [a], Kader Dağcı [a], Murat Alanyalıoğlu [a,b,*]

[a] Atatürk University, Sciences Faculty, Department of Chemistry, 25240 Erzurum, Turkey
[b] Atatürk University, East Anatolian High-Technology Research and Application Center, 25240 Erzurum, Turkey

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ABSTRACT

Potentiostatic and potentiodynamic approaches have been performed for rearrangement of lead sulfide thin films prepared by a successive ionic layer adsorption and desorption technique on Au electrodes. Potentiostatic processes have been applied by potential-controlled electrolyses at −450 mV and potentiodynamic applications have been performed by cyclic voltammetry scanning potential between −800 and 50 mV on lead sulfide modified Au electrodes in pH 5.9 solution. These potential values have been determined by considering underpotential deposition of both lead and sulfur as a result of cyclic voltammetry experiments of lead sulfide modified Au working electrodes. Scanning electron microscopy, scanning tunneling microscopy, and powder X-ray diffraction results show that electrochemical approaches cause a transformation from amorphous to polycrystalline structure for PbS thin films. UV–visible–near infrared spectroscopy investigation of the samples reveals that the optical properties of lead sulfide thin films are protected after electrochemical processes.

1. Introduction

Lead sulfide (PbS) with direct narrow bandgap value of 0.41 eV at 300 K is a very suitable IV–VI semiconductive material for infrared detection, solar cell, Pb^{2+} ion selective sensor, photothermal, and optoelectronic applications. The optical and electrical properties of this semiconductive material are highly related to some factors e.g. crystallinity, particle size, film thickness and surface properties. PbS thin films can be prepared by different techniques e.g. atomic layer epitaxy [1], chemical bath deposition [2], chemical vapor deposition [3], sonochemistry [4], supercritical fluid deposition [5], electrodeposition [6–8], and successive ionic layer adsorption and reaction (SILAR) method [9–11]. Among these techniques, the electrodeposition and SILAR techniques have some advantages. They are simple, quick, non-destructive, environmentally-friendly, and economical techniques. These techniques are operated under ambient conditions and provide thickness control of the deposited films by optimizing deposition cycle for SILAR and by tuning the electrode potential and process time for electrodeposition technique [7,10]. Nevertheless, the SILAR technique generally results with amorphous thin film formation. To overcome this problem, various applications are performed by the researchers. Adding a suitable complexing agent e.g. triethanolamine into cationic precursor is the main application to improve the crystallinity of the material [10]. Another approach used by the scientists is thermal annealing procedure after preparation of semiconductive thin film materials [12].

In this work, we have first time combined SILAR with electrodeposition technique to improve crystallinity of PbS thin films. We have performed potentiostatic and potentiodynamic approaches for the re-organization of PbS thin films prepared by the SILAR technique on Au electrodes. The potentials for electrochemical treatments are determined by considering underpotential deposition (upd) of both lead and sulfur from cyclic voltammetry experiments. Because upd is a surface-limited deposition process, it is supposed that both potentiostatically and potentiodynamically applied processes based on upd of both lead and sulfur provide atom-by-atom orientation and improve the crystallinity of PbS thin films. Characterization of the prepared PbS thin films before and after electrochemical treatments has been carried out by using scanning electron microscopy (SEM), scanning tunneling microscopy (STM), powder X-ray diffraction (XRD), and UV–vis–NIR experiments.

2. Experimental

2.1. Preparation of PbS thin films by SILAR method

All chemicals used for this work have been purchased from

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[*] Corresponding author at: Atatürk University, Sciences Faculty, Department of Chemistry, 25240 Erzurum, Turkey. Fax: +90 442 231 4109.
E-mail address: malanya@atauni.edu.tr (M. Alanyalıoğlu).

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Sigma-Aldrich company. PbS thin films were prepared by using $Pb(CH_3COO)_2 \cdot 3H_2O$ as Pb^{2+} source and $Na_2S \cdot 9H_2O$ (Sigma) as S^{-2} source. 0.05 M lead acetate in 0.1 M acetate buffer solution (ABS) with pH of 5.9 and 0.05 M sodium sulfide in 0.1 M phosphate buffer solution (PBS) with pH of 12.0 were prepared by using Milli-Q ultra pure water (conductivity $\leq 5.5\ \mu S\ m^{-1}$). The ABS was prepared by using $NaCH_3COO$ and CH_3COOH. Na_3PO_4 and Na_2HPO_4 salts were used for the preparation of PBS. The pH of the buffer solutions was adjusted to required pH values by using a Hanna pH-meter with the addition of diluted HCl or NaOH solutions.

A clean substrate was immersed into S^{2-} precursor solution for 20 s, and then rinsed with deionized water for 20 s to remove the unattached ions. Then this sulfur-modified substrate was immersed into Pb^{2+} precursor solution for 20 s and rinsed again with deionized water for 20 s to complete one cycle of SILAR process. The dipping cycle was repeated many times to obtain PbS thin films for electrochemical approaches and the other characterizations. The production process of PbS thin films by the SILAR technique was repeated a number of times and confirmed that reproducible PbS thin films are obtained.

2.2. *Electrochemistry*

The pH of the solutions in an electrochemical cell is a very critical value. If the electrochemical studies are applied at pH values lower than 5.9, sulfur species turns from S^{-2} or HS^- to H_2S (g) form [13]. If pH value of the solution is kept higher than 5.9, soluble Pb^{2+} species starts to precipitate as $Pb(OH)_2(s)$. So, the buffer solution used for investigation of electrochemical properties of PbS thin film was 0.1 M acetate buffer solution with pH of 5.9. Temperature of the electrochemical cell was fixed at 80 °C by using a thermostat system to increase the dissolution of PbS thin films [7]. The solutions were deoxygenated by passing dry nitrogen through the electrochemical cell for at least 15 min prior to each electrochemical study. Electrochemical investigation of PbS thin films was achieved by using either potentiodynamic (cyclic voltammetry) or potentiostatic (potential-controlled electrolysis) techniques, with an Epsilon (BASi) potentiostat system connected to a three electrode cell. Current–time (i–t) transients were obtained from potentiostatic application of PbS/Au electrodes in 0.1 M acetate buffer (pH: 5.9) solution. Electrochemical studies were carried out by using different working electrodes. Polycrystalline Au electrode was performed as working electrode to determine upd potential values of both lead and sulfur. PbS thin films were prepared on single crystal Au(111) working electrodes because Au(111) has an atomically flat surface and can be used as a reference surface to monitor changes on the surface. Indium tin oxide coated glass (ITO) working electrodes were preferred for optical characterization of the thin films due to its optically transparent properties.

Single crystal Au(111) substrates were prepared as previously described [14]. Briefly, polycrystalline Au wires (Alfa Aesar, 99.999% purity, 1.0 mm diameter) were molten in H_2 flame to obtain ball formed at the end of Au wire. This ball-shaped Au electrode contains a few large (111) facets that are visible by eye. Surface area of these facets is lower than 1 mm^2. Prior to each electrochemical experiment, polycrystalline gold electrodes were flame-annealed in H_2 flame for about 30 s, and after a short time cooling in air, the electrodes were quenched in Milli-Q water. This procedure was repeated at least five times. Au(111) single crystal substrates with surface area around 5 mm^2 were prepared for especially powder XRD characterization of PbS thin films by polishing them parallel to (111) direction [15]. The polycrystalline regions of the prepared substrates were covered by an electrochemically inert epoxy (Epoxy-Patch) to carry out electrochemical measurements on Au(111) electrodes. ITO electrodes were cleaned by sonication in detergent solution for 5 min and then rinsed with a large amount of doubly distilled water. Further sonication in ethanol for 5 min was applied before being blown dry with an argon stream. In all cases, an Ag/AgCl (3 M NaCl) (BASi) electrode served as reference electrode and a Pt wire was used as counter electrode.

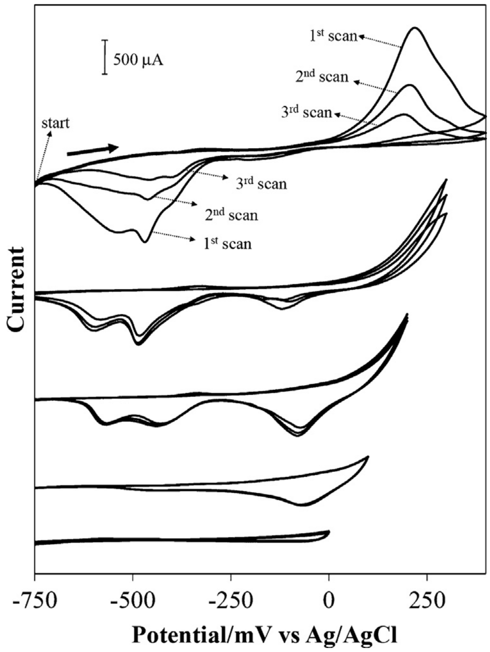

Fig. 1. Consecutive cyclic voltammograms of PbS/Au working electrode in 0.1 M ABS (pH: 5.9). Potential scan starts at −750 mV and cycling is applied from different positive potentials of 0, 100, 200, 300, and 400 mV. Cell temperature: 80 °C, scan rate: 50 mV s^{-1}.

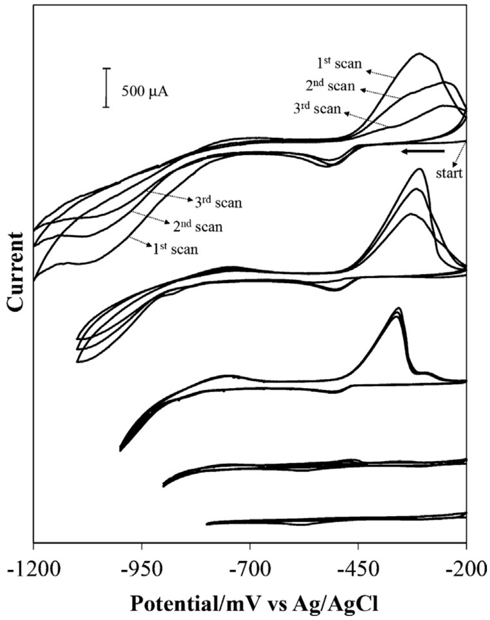

Fig. 2. Consecutive cyclic voltammograms of PbS/Au working electrode in 0.1 M ABS (pH: 5.9). Potential scan starts at −200 mV and cycling is applied from different negative potentials of −800, −900, −1000, −1100, and −1200 mV. Cell temperature: 80 °C, scan rate: 50 mV s^{-1}.

2.3. *Instrumentation*

Morphological investigation of PbS thin films was performed in