Characterization of size-quantized PbTe thin films synthesized by an electrochemical co-deposition method

İbrahim Y. Erdoğan a, Tuba Öznülü a, Ferhat Bülbül b, Ümit Demir a,⁎

a Atatürk University, Arts and Sciences Faculty, Department of Chemistry, 25240, Erzurum, Turkey
b Atatürk University, Engineering Faculty, Department of Mechanical Engineering, 25240, Erzurum, Turkey

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A B S T R A C T
Size-quantized thin films of PbTe were electrodeposited on Au (1 1 1) substrates using a practical electrochemical method, based on the simultaneous underpotential deposition of Pb and Te from the same solution containing ethylenediamine tetraacetic acid, Pb2+, and TeO32− at a constant potential. These thin films were characterized by X-ray diffraction (XRD), scanning tunneling microscopy (STM), atomic force microscopy (AFM), energy dispersive spectroscopy (EDS), and reflection absorption-FTIR (RA-FTIR). AFM, STM, and XRD results indicate that the growth of PbTe thin films follows the nucleation and two dimensional growth mechanism, resulting in high crystalline films of PbTe (2 0 0) in cubic structure, which was grown at a kinetically preferred orientation on Au (1 1 1). The EDS analyses of the films reveal that Pb and Te are present in an atomic ratio of approximately 1:1. The quantum-confined effect of the PbTe thin films are confirmed by the RA-FTIR measurements.

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1. Introduction

Lead chalcogenides (PbS, PbTe, and PbSe) are narrow band-gap semiconductors largely used in thermoelectric (TE) and infrared (IR) applications [1,2]. It has been reported that PbTe and PbTe-based compounds are superior materials for solid-state TE cooling and electrical power generation devices [3,4]. Ultrathin films of compound semiconductors exhibit different electronic, magnetic, optical, chemical, and mechanical properties that cannot be obtained in their bulk counterparts due to their quantum confinement effects. Strong quantum confinement effects in IV–VI compound semiconductors are well known [5–8]. As quantum confinement effects play a key role in modern surface science, the deposition of nanostructures or nanometer thin films of PbTe has also become a target of major interest. Various methods such as molecular beam epitaxy [9], vacuum evaporation [10], hot-wall epitaxy [11], electrodeposition techniques [12–14] etc. have been used for the preparation of PbTe films. Of all the deposition techniques, electrodeposition is a simple, quick and economical method for the preparation of thin films. Recent studies in this field have focused on achieving atomic-level control of the growth process, leading to the formation of well-ordered deposits of the desired material. Stickney et al. [14,15] constructed an electrochemical analog of the conventional atomic layer epitaxy (ECALE), which has been used to produce a wide variety of well-ordered semiconductor deposits [16–20]. In ECALE, surface limited reactions through underpotential deposition (UPD) are used to synthesize a compound by depositing each element from their separate solutions. Nicolau et al. [21] developed a method called successive ionic layer adsorption and reaction (SILAR), which attempts to grow thin films of CdS by repeating the sequential immersion of substrate into the solution of Cd2+ and S2− with rinsing by water in between. One disadvantage of ECALE and SILAR is that the electrode needs to be rinsed after each deposition cycle, which may result in a waste of time and chemicals. Recently, we have developed an electrochemical process, based on the co-deposition from the same solution at the UPD of the precursors of the target compound, which have been used for the electrochemical deposition of PbS, ZnS and CdS in the single crystal form [22–24].

In this paper, we report on the growth of PbTe films on single crystalline Au (1 1 1) by an electrochemical co-deposition method, through a one-step process. In order to determine the morphological and structural characteristics, the deposited films were examined by using X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Reflection absorption-FTIR (RA-FTIR) measurements as a
function of the film thickness were used to study the optical and electronic properties of the electrodeposited PbTe thin films.

2. Experimental section

2.1. Chemicals

All the electrolyte solutions were prepared from reagent grade chemicals and deionized water (resistivity > 18 MΩ cm). Prior to each electrochemical experiment, the working solution was deaerated with bubbling N₂ for 15 min. Ethylenediaminetetraacetic acid (EDTA) was used to form a PbEDTA complex in order to prevent the spontaneous precipitation of Pb²⁺ as Pb(OH)₂. PbTe electrodeposition was carried out from a 0.0001 M TeO₂ (Merck), 0.3 M Pb(CH₃COO)₂·3H₂O (Merck), and 0.32 M EDTA disodium salt (C₁₀H₁₄N₂Na₂O₈·2H₂O, Merck) solutions. The pH value of the solution was adjusted to 9 using NaOH.

2.2. Electrochemistry

Electrochemical measurements were carried out in a conventional three-electrode cell system (C3 Cell Stand, BAS) under an N₂ atmosphere, at room temperature with a BAS 100B/W Electrochemical Workstation. The working electrode was a (1 1 1)-oriented single-crystal gold (Johnson Matthey, 99.999%) prepared with a pure gold wire in hydrogen–oxygen flame. A platinum wire was used as a counter electrode. All the potentials were referenced to a 3 M Ag/AgCl reference electrode.

2.3. Characterization of materials

The optical absorbance spectra of the electrochemically deposited PbTe films on Au Plates were measured using a variable angle reflection rig in conjunction with a Perkin–Elmer Spectrum One FT-IR spectrometer in the spectral range of 2000–7800 cm⁻¹ at room temperature. The measurements were obtained by an average of 100 scans and a resolution of 4 cm⁻¹. XRD experiments for films on Au(111) were performed in a Rigaku Advance Powder X-ray Diffractometer instrument using Cu K radiation (=1.5405 Å), operating at 30 kV and 30 mA over a 20 range of 20°–60°. The XRD phases present in the samples were identified with the help of the Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data (JCPDS-ICDD). The elemental compositions (Pb/Te) of the PbTe deposits were determined by EDS with a JEOL-6400 system coupled to the scanning electron microscope. The operating conditions for EDS analysis include an accelerating voltage of 15 kV, a beam current of 5 nA, a working distance of 15 mm, and a live time of 60 s for each run. The surface morphologies of the films were inspected by contact mode (CM)-AFM and constant current mode STM (PicoSPM, Molecular Imaging Inc.). All images were taken in air. 450 μm long silicon nitride cantilevers with a spring constant of 0.58 N/m and a resonant frequency of 13 kHz for CM-AFM were used. Typical tunneling current and applied voltages for STM imaging were 0.5 nA and 1–2 V, at scan rates of 2 Hz. Tungsten and Pt–Ir tunneling probes were employed. AFM/STM images were taken in different zones of the films to check their homogeneity.

3. Results and discussion

3.1. Electrochemical deposition

Fig. 1a presents a cyclic voltammogram of an Au (1 1 1) electrode immersed in 0.1 mM TeO₂ in 0.32 M EDTA supporting electrolyte at the UPD region of Te. The anodic stripping peak, labeled A (around 295 mV), is associated with the two cathodic deposition peaks, labeled C₁ and C₂ (around —500 and —590 mV, respectively). That the bulk Te deposition does not occur until —700 mV in the pH 9 solution suggests that surface limited atomic layers of Te might be formed at potentials in the range of —590 (C₁) to —700 mV. These observations are very similar to those obtained in acidic solution by us [25] and others [26,27]. Fig. 1b shows the cyclic voltammogram for Pb UPD on the Au (1 1 1) surface in the deposition containing 0.3 M Pb²⁺ ions in the presence of 0.32 M EDTA. This voltammogram contains only one redox couple corresponding to the deposition and stripping of Pb atomic layers. The anodic stripping peak, labeled A (around —360 mV), is associated with the cathodic deposition peak, labeled C (around —625 mV). This behavior has been confirmed in a detailed investigation of Pb UPD in EDTA solutions on Au (1 1 1) recently carried out in our laboratory. The bulk Pb deposition in the pH 9 solution does not occur until —900 mV. Fig. 1c shows the overlapped cyclic voltammograms of Te UPD and Pb UPD in 0.32 M EDTA solutions. If the potential of the working electrode was kept constant at a potential between the reductive UPD wave of Pb²⁺ and bulk wave beginning of TeO₂⁻⁻(Te⁴⁺) (between the dotted lines), Pb and Te would deposit underpotentially at the electrode surface. These underpotentially deposited Pb and Te atoms react to form the PbTe compound semiconductor. Therefore, it should promote the electrochemical atom-by-atom growth of PbTe at the substrate surface, while keeping Pb as a complexed form so that the formation of PbTe particles in the solution
3.2. Electronic properties of PbTe thin films

Band gaps of electrodeposited PbTe thin films were determined by RA-FTIR measurements. Fig. 2 presents the absorption spectra of PbTe obtained in the range of 7800–2660 cm\(^{-1}\) at different deposition times. The absorption edges measured for the 1, 3, 5, 6, 8, 10, 12 and 15 h deposits were 6760, 6360, 5240, 4830, 4430, 3870, 3060 and 2660 cm\(^{-1}\), respectively. The absorption edges were red-shifted from 6760 cm\(^{-1}\) (1 h) to 2660 cm\(^{-1}\) (15 h) with an increase in the film thickness towards the characteristic values of those of the bulk materials. The band-gap values were determined by linear extrapolation to the X-axis (h\(\nu\)) from the straight part of the curve. As shown in Fig. 3, the band gap decreased with an increase in deposition time. It has been reported that PbTe is a compound-semiconductor with a direct band gap and therefore, the plots of \((\alpha h \nu)^{1/2}\) versus \(h \nu\) should be a straight line and the intercepts on energy axis would give the band gap of the film [28]. The band gaps of PbTe thin films electrodeposited for 15 and 1 h were found to be 0.33 and 0.84 eV, respectively. The band gap (0.33 eV) of the 15 h electrodeposited film resembles the value for the band gap energy of the bulk PbTe [10]. The PbTe film thickness can be determined using the charge obtained by coulometric measurements in conjunction with Faraday’s law:

\[
t = \frac{MQ}{nFA}
\]

where \(t\) is the film thickness, \(M\) is the molecular weight (334.8 g/mol for PbTe), \(Q\) is the charge passed, \(\rho\) is the density (8.16 g/cm\(^3\) for PbTe), \(F\) is Faraday’s number (96485 C/Equivalent), \(n\) is the charge number (6), and \(A\) is the surface area of electrode (1 cm\(^2\)). A representation of the reactions occurring at the working electrode is shown below.

\[
\text{Pb}^{2+} + \text{TeO}_2^{5-} + 4\text{H}_2\text{O} \rightarrow \text{PbO}_{2.5}^{2+} + 4\text{e}^- + 4\text{OH}^-
\]

In Eq. (2), six equivalents of charge must be passed in order to produce 1 mol of PbTe. Table 1 summarizes the band gap dependency of PbTe thin films as a function of the deposition time, the number of coulombs passed during the electrodeposition, and the film thickness. The band gap decreases as the deposition time increases. Fig. 4 shows a plot of the experimentally determined band gaps and theoretically calculated band gaps using the Eqs. (3) and (4) as a function of the thickness of the PbTe films. The band gap of semiconductor films with infinite potential barriers at the interfaces is theoretically given by Eq. (3), as a function of the film thickness [29,30]:

\[
E_g^* = E_g + \frac{\hbar^2}{2m_e^*} \left( \frac{8\mu a^2}{\hbar^2} \right) - E_{\text{bin}}
\]

where \(E_g\) is the band gap of bulk PbTe, \(d\) is the film thickness, \(m_e^*\) and \(m_h^*\) are the effective mass of an electron and a hole, respectively, and \(E_{\text{bin}}\) is the binding energy of the lowest exciton already estimated as a function of the film thickness. Experimentally determined band gaps are in good agreements with the calculated band gaps of PbTe thin films for thicknesses greater than 25 nm; however, they disagree for thicknesses smaller than 25 nm. Torimoto et al. observed a similar discrepancy in the band gap for the electrochemical deposition of CdS and ZnS on Au substrates [29,30]. These deviations in band gap values for thinner films are caused by the leakage of electrons outside the film since the depositions are carried out on conducting Au substrates. The very large Bohr radii in lead materials (20–46 nm), as opposed to smaller Bohr radii systems, allow an evaluation of their optical properties within the limit of extremely strong quantum confinement. These Pb-VI compounds have large Bohr radii, 20 nm for PbS, 46 nm for PbTe and PbSe [31]. This value roughly agrees with the experimentally obtained critical bulk

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**Table 1**

<table>
<thead>
<tr>
<th>Deposition time (hour)</th>
<th>Charge (mC/cm(^2))</th>
<th>Band gap (eV)</th>
<th>Thickness (nm)</th>
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</thead>
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<tr>
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<td>0.84</td>
<td>0.8</td>
</tr>
<tr>
<td>3</td>
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<td>0.79</td>
<td>5.0</td>
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<td>5</td>
<td>15.23</td>
<td>0.65</td>
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<td>23.53</td>
<td>0.60</td>
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<tr>
<td>8</td>
<td>33.26</td>
<td>0.55</td>
<td>25.0</td>
</tr>
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<td>0.48</td>
<td>34.9</td>
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<tr>
<td>15</td>
<td>64.87</td>
<td>0.33</td>
<td>46.0</td>
</tr>
</tbody>
</table>

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**Fig. 2.** RA-FTIRS of PbTe thin films deposited on Au substrates at different deposition times. The absorbances of the individual spectra have been rescaled to enhance comparison.

**Fig. 3.** Plots of \((\alpha h \nu)^{1/2}\) versus \(h \nu\) for the PbTe thin films deposited on Au \((1 1 1)\) at different deposition times.

**Fig. 4.** Plots of \((\alpha h \nu)^{1/2}\) versus \(h \nu\) for the PbTe thin films deposited on Au \((1 1 1)\) at different deposition times.
thickness of PbTe thin films. The expected increase in the band gap is observed as the film thickness decreases. These results clearly demonstrate that the band gap of the materials is directly related to the film thickness [32]. The evident blue shift in the absorption spectrum of our films stems from a quantum confinement of the electron-hole pair caused by the small particle size or ultra thin film thickness.

3.3. Morphological and structural characterization of PbTe thin films

Fig. 5a shows the STM image of the initial stages of the nucleation and growth of PbTe electrodeposited at $-650$ mV for 15 min. Evenly distributed nano-seeds of approximately the same size are observed on the surface of the Au (1 1 1) electrode. The height profile (trace of the vertical $z$ position of the tip) across a grain is indicated by an arrow in the lower panel of Fig. 5a. Most nanoparticles have a uniform width and thickness in the ranges of 10–15 nm and 5–7 Å, respectively. As the time for deposition increases to 1 h, nanoparticle diameters increase and the other particles form at the surface but the thickness stays constant (Fig. 5b). The subsequent growth is governed by the lateral growth. Finally, one can observe a complete growth of the first layer that seems to be almost fully closed at 2 h. The line scan profile across the deposit in Fig. 5b obviously indicates a two-dimensional (2-D) nucleation and growth of PbTe thin films, which are imaged with a thickness of 0.5–0.7 nm. Fig. 6 shows two AFM images obtained after the electrodeposition of PbTe for 6 and 15 h. The crystallite sizes of PbTe films electrodeposited for 6 and 15 h were about 70 and 200 nm in diameter and 60 to 150 nm in thickness, respectively. Fig. 7 shows the XRD patterns of the electrodeposited films on Au (1 1 1) substrate prepared at different deposition times. For a comparison, the relative intensities of the diffraction peaks from the standard card pertaining to PbTe [33] and Au [34] were labeled on the bottom of Fig. 7 as well. The XRD diffractogram of PbTe electrodeposited for 6 h consists of a strong diffraction peak at 27.6° (2θ scale) arising from (2 0 0) reflections from PbTe and a strong peak at 38.2° arising from the (1 1 1) reflections of Au, which belongs to a single crystalline substrate in this study. The weaker diffractions at 39.5° and 57.1° correspond to (2 2 0) and (4 0 0) reflections of PbTe, respectively. As the deposition time is increased to 15 h (Fig. 7b), the intensity of the Au (1 1 1) reflections decreases and the intensity of PbTe (2 0 0) increases, while diffractions along (2 2 0) and (4 0 0) become almost invisible. This indicates that the crystallites in the film have a preferred growth in this direction. The (2 0 0) reflections of PbTe electrodeposited for 6 and 15 h gave full width at half-maximum values of 0.35° and 0.18°, respectively. These results indicate that highly crystalline deposits of PbTe can be grown at a kinetically preferred orientation on Au (1 1 1) due to controlled growth processes associated with low deposition rates. It has been shown that a low nucleation rate and kinetic control growth of PbTe deposits result in a single crystal of PbTe with (110) preferred orientation [32]. Our observations indicate that single crystals of PbTe with a preferred orientation form when electrodeposition is carried out at a low deposition potential and the low concentration of precursors results in longer deposition times.

The average crystallite sizes of the PbTe nanoparticles were determined from the width of the reflection peaks according to the Debye–Scherrer equation. By applying this equation to the line broadening of the (2 0 0) peak in Fig. 7a, the crystallite size was estimated as 41 nm for the films deposited for 6 h. However the average particle size analysis of AFM image (Fig. 6a) recorded for the same duration gives a mean diameter of 70 nm, which is larger than the particle size in XRD measurements. The discrepancy between the particle size obtained from the XRD and AFM measurements suggest that the observed structures in the AFM image are composed of...
smaller PbTe crystallites. Similar deviations in particle size from the XRD and AFM measurements are observed for Fe₂O₃ crystallites [35].

The electrodeposition of PbTe thin films was first reported by Saloniemi et al. [13]. They observed that smooth, dense Te-rich PbTe thin films with a relatively (2 0 0) preferred crystal orientation. Mondal's group reported that the electrochemical deposition of PbTe thin films were polycrystalline in nature with a cubic phase [36]. Beaunier et al. investigated the electrochemical deposition of films onto (111) InP single crystal substrates [37]. They reported that the as-deposited PbTe films had poor epitype due to the high polycrystallinity. Ivanova et al. used n-Si (1 0 0) wafers as a substrate for the electrodeposition of PbTe films [38]. They found that the nucleation and growth mode of PbTe was determined to be 3D progressive nucleation under the diffusion control. X-ray diffraction patterns indicated PbTe thin film had (2 0 0) preferred crystal orientation. However, XRD studies obtained in our method indicates that the preferred crystal orientation at (2 0 0) is more dominant than the ones obtained by the above electrochemical methods. There are also some chemical routes for the synthesis of PbTe thin films in literature [39–42]. PbTe thin films deposited by these methods were polycrystalline in nature and have no preferred orientation.

The elemental compositions (Pb/Te) of the electrodeposited PbTe thin films were determined by the EDS technique. We observed two weak X-ray emissions corresponding to Pb and Te. Intense Au emission from the substrate is also observed. The absence of any other peaks indicates that the PbTe films are homogeneous in composition and formed from Pb and Te. EDS analyses of different regions of the electrodeposited PbTe samples on Au substrate gave the same results. For the deposited PbTe thin films, the quantitative atomic ratio of Pb and Te are approximately 49% versus 51%, which is close to 1:1 stoichiometry.

4. Conclusions

We have shown that the PbTe thin films can be prepared electrochemically at room temperature from the same solution containing EDTA, Pb, and Te on the single crystal gold substrate at a constant potential. In addition, the results obtained in this study suggest that the thickness of the PbTe thin films can be controlled by the deposition time. Morphology and structure analyses confirm the superior quality of the thin film semiconductors prepared by this technique, in comparison to alternative electrochemical procedures. The EDS analyses indicate that the lead to telluride ratio in the films is close to 1:1. The XRD analyses demonstrate that PbTe on Au (1 1 1) is of a single crystal structure with a dominant (2 0 0) orientation. The morphological investigation of PbTe thin films revealed that the film growth follows a 2-D nucleation and growth mechanism. A highly strong quantum confinement effect was observed for PbTe deposits. Decreasing the time for the electrodeposition of PbTe leads to a sharp decrease in the absorption wavelength, which causes a high blue shift in the band-gap of the semiconducting material.

Acknowledgments

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References