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

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ABSTRACT

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, Pb^{2+}, and TeO_3^{2-} 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.

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 of 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 Cd^{2+} and S^{2-} 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

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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 N_2 for 15 min. Ethylenediamine tetraacetic acid (EDTA) was used to form a PbEDTA complex in order to prevent the spontaneous precipitation of Pb^{2+} as $Pb(OH)_2$. PbTe electrodeposition was carried out from a 0.0001 M TeO_2 (Merck), 0.3 M $Pb(CH_3COO)_2 \cdot 3H_2O$ (Merck), and 0.32 M EDTA disodium salt ($C_{10}H_{14}$ $N_2Na_2O_8 \cdot 2H_2O$, 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 N_2 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 k V and 30 m A over a 2θ 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 k Hz 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 TeO_2 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 C_1 and C_2 (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 (C_2) 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 solution containing 0.3 M Pb^{2+} 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 Pb^{2+} and bulk wave beginning of TeO_3^{2-}(Te^{4+}) (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

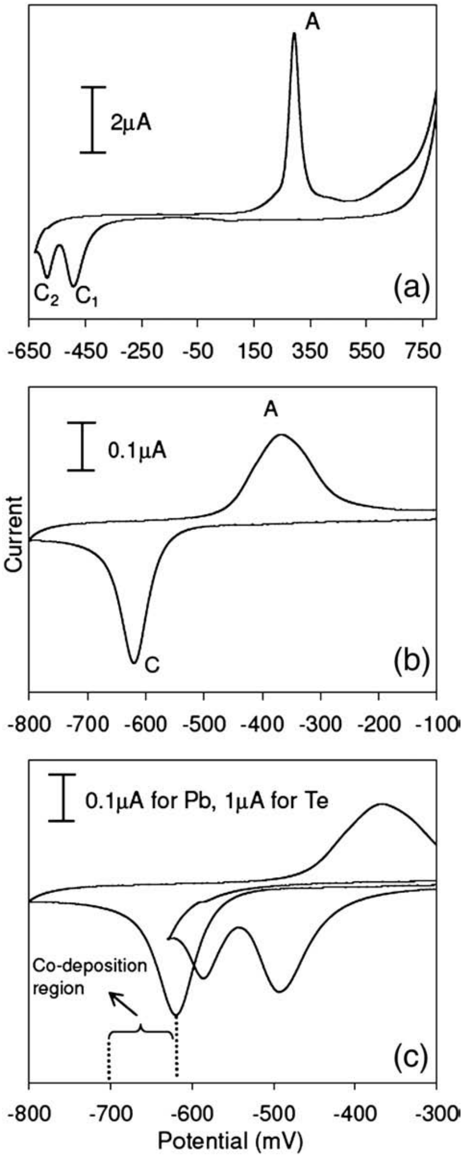

Fig. 1. Cyclic voltammogram of Au (1 1 1) substrate in the solution containing (a) 0.0001 M TeO_2 and 0.32 M EDTA; (b) 0.3 M $Pb(CH_3COO)_2$ and 0.32 M EDTA; and (c) overlapped voltammograms shown in (a) and (b) at 25 mV/s.