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Electrodeposition of a PbTe/CdTe superlattice by electrochemical atomic layer deposition (E-ALD)

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ABSTRACT

A PbTe/CdTe superlattice was deposited using the electrochemical form of atomic layer deposition (E-ALD). The E-ALD program consisted of 15 periods of 5 cycles of CdTe and 15 cycles of PbTe, grown on a 15 cycle PbTe pre-layer formed on 200 nm of Au vapor deposited on glass. The cycle used for CdTe nanofilm formation involved ramped potentials, that is, the potentials used to deposit Cd and Te were incremented negatively for each of the first 20 cycles. After 20 cycle the potentials were held constant for all the remaining cycles, and resulted in a stoichiometric and homogeneous CdTe deposit, as shown by Electron Probe Microanalysis (EPMA). Peaks corresponding to the cubic phase of CdTe were observed in the XRD pattern of the CdTe, with the (111) dominant. Optical studies of the CdTe revealed a band gap of 1.5 eV. The PbTe/CdTe superlattice was formed using the period above fifteen times. Deposition potentials, current–time traces and elemental coverages are described. The superlattice was determined to be stoichiometric, as determined by EPMA. The superlattice X-ray diffraction pattern displayed satellite peaks on the (111) peak, as symmetric shoulders, indicating a period of 11 nm, rather than the anticipated 6 nm.

1. Introduction

CdTe and PbTe are both compound semiconductors, denoted as II–VI and IV–VI respectively. Both have been extensively studied and grown by a variety of techniques: close sublimation [1], co-evaporation [2], chemical synthesis [3], rf sputtering [4], molecular beam epitaxy [5], organometallic vapor epitaxy [6], pulse laser deposition [7], co-deposition [8] and electrochemical atomic layer deposition (E-ALD) [9]. They are important in photovoltaic devices, optoelectronic devices, radiation detectors, laser materials, thermoelectric materials, sensors and various other electronic devices [3,5b,8a,10]. CdTe is one of the semiconductors of choice for photovoltaics because of its high absorption coefficient ($>10^4\ \mathrm{cm}^{-1}$) and an optimum direct band gap at 1.5 eV, ideal for single junction photovoltaic cells. PbTe is an important thermoelectric material [11], with a rock salt structure, a narrow band gap ($E_g = 0.29$ eV) and a high absorption coefficient ($\sim 10^{-4}\ \mathrm{cm}^{-1}$). The lattice constants for CdTe and PbTe are nearly identical, with values of 0.648 Å and 0.646 Å for CdTe and PbTe respectively. Both compounds are cubic, but with different structures: zinc blende and rock salt. Both of these materials have been formed using E-ALD, and this work was undertaken to investigate the formation of a lattice matched superlattice using E-ALD. The large difference in band gaps between the compounds should allow band gap engineering by changing the superlattice period [12]. Ideally, a lattice mismatch of less than 1% and keeping the component nanofilms thinner than the critical thickness results in the highest quality superlattices [12,13]. The lattice constants for CdTe and PbTe suggest a lattice mismatch of only ~0.3%. The formation of PbTe/CdTe superlattices have been investigated [14] for probable use a heterosystem for optoelectronic devices [14i]. The majority of the reports of the growth of PbTe/CdTe heterosystems made use of molecular beam epitaxy (MBE). E-ALD as a superlattice growth method with atomic layer control is considerably less costly.

This report concerns the formation of a PbTe/CdTe superlattice using electrochemical atomic layer deposition (E-ALD), the electrochemical analog of atomic layer deposition (ALD) [15]. ALD involves the use of surface limited reactions to form a material an atomic layer at a time. The vast majority of ALD is performed using methods related to chemical vapor deposition (CVD), in vacuum. Surface limited reactions are achieved by control over the substrate temperature and alternating exposure to pulses of two reactants. Great success has been had in the formation of some important oxides. The requirement for volatile reactants has made the formation of many compounds more difficult, as organometallic precursors have been tried and can result in carbon contamination.

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In electrochemistry, surface limited reactions are referred to as under potential deposition (UPD), a phenomenon where an atomic layer of one element is deposited on the second, at a potential prior to (under) that needed to form the bulk element [16]. By controlling the solution in contact with the deposit and the potential of the electrode, atomic layers can be deposited, under equilibrium conditions, by electrodeposition. E-ALD is the use of UPD in an ALD cycle. It is generally performed at or near room temperature, which limits interdiffusion, which is beneficial in the formation of a superlattice. Besides atomic layer control, E-ALD has the advantage over conventional electrodeposition because the process is broken into a sequence of individually controllable steps, which can be separately optimize. Historically, electrodeposited compounds [17] require annealing after deposition to achieve a reasonable XRD pattern, while experience has shown that most compounds formed using E-ALD display XRD patterns without annealing [9e,13b,18].

In the studies reported here of CdTe nanofilms and a PbTe/CdTe superlattice, the deposition potentials for Pb, Te and Cd were ramped for the first 5–30 E-ALD cycles. Possible reasons for the use of "potential ramping" over the first few cycles have been reported and discussed previously [9e,18a,19].

2. Experimental

An automated flow electrodeposition system (Electrochemical ALD L.C., Athens, GA) consisting of a of solution reservoirs, computer controlled pumps, distribution valve, potentiostat and a electrochemical flow cell and was used to grow CdTe nanofilms and a PbTe/CdTe superlattice. The reference electrode was Ag/AgCl (3 M NaCl) (Bioanalytical systems, Inc., West Lafayette, IN) and the auxiliary electrode was an Au wire embedded into the Plexiglas flow cell. The cell volume was about 0.3 mL, solutions were pumped at 40 mL/min, and the deposition area of the electrodes used in these experiments was 4 cm^2. The flow cell was designed to promote laminar flow. The system was contained within a nitrogen purged Plexiglas box to minimize oxygen during electrodeposition.

Substrates used consisted of 200 nm of Au vapor deposited on 3 nm of Ti, on glass microscope slides, held at 250° during growth. The glass slides were then annealed in the deposition chamber at 400 °C for 12 h, while the pressure was maintained at 10^{-6} Torr.

Reagent grade or better chemicals were used with water from a Nanopure water filtration system fed by the house deionized water, to prepare the different solutions used in this study. The lead solution consisted of 0.5 mM $Pb(ClO_4)_2$ (Alfa Aesar, Ward Hill, MA), pH 3, with 0.1M $NaClO_4$ (Fischer Scientific, Pittsburgh, PA) as the supporting electrolyte. The cadmium solution was made of 0.5 mM $CdSO_4$ (Alfa Aesar, Ward Hill, MA), pH 3, with 0.1M $NaClO_4$ (Fischer Scientific, Pittsburgh, PA) as the supporting electrolyte. The tellurium solution was made 0.5 mM TeO_2 (Alfa Aesar, Ward Hill, MA), pH 9.2, buffered with 50.0 mM sodium borate and 0.1M $NaClO_4$ (Fischer Scientific, Pittsburgh, PA) as the supporting electrolyte. A pH 3 blank solution of 0.1M $NaClO_4$ (Fischer Scientific, Pittsburgh, PA) was used as well. NaOH and $HClO_4$ (Fischer Scientific, Pittsburgh, PA) were used to adjust the pH values of all the solutions.

The E-ALD cycle program used to grow CdTe was: Te solution flushed into the cell for 2 s at the chosen potential, then the solution was held quiescent for 15 s in the cell for deposition. The blank solution was then flushed through the cell at the same potential for 3 s to rinse out excess TeO_3^{2-} ions. The Cd solution was then flushed through the cell for 2 s at the selected Cd deposition potential, and held quiescent for 15 s for deposition. Blank solution was again flushed through the cell for 3 s to rinse out excess Cd^{2+} ions, completing one E-ALD cycle for CdTe. This cycle was repeated as many times as needed to form CdTe deposits of the desired thickness.

The E-ALD cycle used to form PbTe consisted of: Te solution flushed into the cell for 2 s at the chosen potential, then held quiescent for 15 s for deposition. The blank solution was flushed through the cell at the same potential for 3 s, to rinse out excess TeO_3^{2-} ions. The Pb solution was then flushed through the cell for 2 s at the Pb potential, and held quiescent for 15 s for deposition. Blank solution was again flushed through the cell for 3 s to rinse out excess Pb^{2+} ions, completing one PbTe E-ALD cycle. The cycle was repeated as many times as needed to form PbTe nanofilms of the desired thickness.

Wavelength dispersive X-ray analysis (EPMA) of the samples were performed with a Joel JXA-8600 electron probe. Glancing angle X-ray diffraction patterns were obtained on a Scintag PAD V diffractometer, equipped with a parallel plate collimator on the detector, to improve resolution in the asymmetric diffraction configuration. The absorption measurements were taken at normal incidence, over the wavelength range of 1100–500 nm in 1 nm decrements, for a total of 1200 s, using an Oriel Cornerstone 260 1/4 m monochromator spectrometer.

3. Results and discussion

To better develop cycles for CdTe and PbTe/CdTe, the electrochemical behavior of the Au on glass electrodes in the Te, Cd and Pb solutions was investigated using cyclic voltammetry (CV). Fig. 1(a and b) shows CVs in the 0.5 M $HTeO_2^+$, which have been discussed in previous work [9e]. The reductive peaks in the negative going scans and their corresponding oxidative features in the 1st

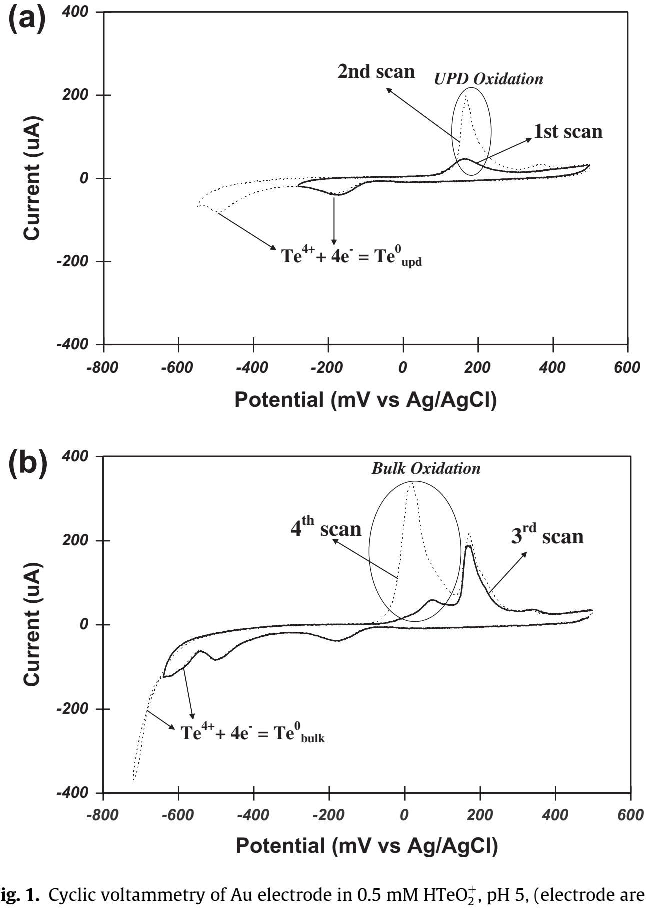

Fig. 1. Cyclic voltammetry of Au electrode in 0.5 mM $HTeO_2^+$, pH 5, (electrode area: 4 cm^2, scan rate: 10 mV s^{-1}).