## ELECTRODEPOSITION OF NANOSTRUCTURES BY ELECTROCHEMICAL ATOMIC LAYER EPITAXY (EC – ALE)

by

#### MAHLANYANE KENNETH MATHE

(Under the direction of John. L. Stickney)

#### ABSTRACT

An automated flow deposition system was used in the electrodeposition of II-VI and IV-VI thin films and nanostructures by electrochemical atomic layer epitaxy (EC-ALE). The II-VI compounds studied were CdSe, HgSe, CdSe/HgSe and HgTe. PbSe thin films and PbTe/PbSe nanostructures were the IV-VI compounds studied. Cyclic voltammograms were used to establish a range of underpotential (upd) deposition potentials for all the systems presented here in these studies. EC-ALE exploits the use of surface limited reactions, underpotential deposition (upd) to deposit thin films one layer at a time on Au substrates.

Upd is a well-documented phenomenon in which one element deposits onto another element at a potential prior to (under) that necessary to deposit the element onto itself. The resulting deposit is limited to an atomic layer.

CdSe thin films were studied to optimize the deposition program and simplify the precursor solutions. 200 cycle deposits were formed with reproducibility and were characterized by: X-ray diffraction (XRD) for the crystal structure and Atomic Force Microscopy (AFM) for the morphology. Electron Probe Microanalysis (EPMA) was used to determine the stoichiometry, with deposit thicknesses measured by Ellipsometry. The bandgap were

determined by ultraviolet spectroscopy (UV-VIS), photoconductivity, or absorption (FTIR) measurements. Other compounds formed were also characterized, FT-IR only, plus EPMA, XRD and AFM.

PbSe thin films were modeled for quantum confinement using effective mass approximations for the hyperbolic and parabolic band models. The dependence of the bandgap on the thickness of the films was described as well.

INDEX WORDS: EC-ALE, Electrodeposition, cyclic voltammograms, upd, CdSe, HgSe,
 HgTe, CdSe/HgSe, PbSe, PbTe/PbSe, automated flow deposition system,
 Au substrates, XRD, AFM, FTIR, UV-VIS, Ellipsometer, Bandgap,
 EPMA, SEM, Photoconductivity

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### DEDICATION

To the Queen and King of my life, Mom and Dad, even though you never went to High School, you have always encouraged me about the importance of education. For that I want to say thank you. I would like to dedicate this work to my wife Piliswa, my daughter, Selloane and my son, Mandla. Your sacrifices are deeply appreciated and from this moment I devote my life to you.

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"Making the simple complicated is commonplace; making the complicated simple, awesomely simple, that's creative." - Charles Mingus

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## CHAPTER 1

### INTRODUCTION AND LITERATURE REVIEW

Nanometer scale semiconductor structures, (nanostructures) exhibit interesting optical, electrical and magnetic properties manipulated by changing their physical dimension. [1, 2]. Nanostructured materials are an emerging interdisciplinary field [3], and can be formed by various methods. The fabrication of electronic and optoelectronic devices requires high quality compound semiconductor thin films. The major semiconductor growth methodologies that have been used to form high quality semiconductor thin films are chemical vapor deposition (CVD) [4-6] and molecular beam epitaxy (MBE) [7-9]. However, these gas phase methods require expensive equipment and use toxic precursors. The electrochemical formation of thin film semiconductors greatly advanced by development of codeposition by Kröger [10], and used to form CdTe. However, codeposition is limited by a lack of control during the deposition process, resulting in mostly polycrystalline deposits.

Atomic Layer Epitaxy (ALE) developed by Suntola [11] became a promising method because the deposition process could be controlled. ALE used surface limited chemical reactions in a deposition cycle. The deposition cycle may be repeated to form thin films of any thickness.

The studies on electrochemical atomic layer epitaxy (EC-ALE) are divided into: fundamental studies using ultra-high vacuum surface analysis methods (UHV-EC); thin layer electrode (TLE) studies using cyclic voltammetry; electrochemical scanning tunneling microscopy (EC-STM); electrochemical quartz crystal microbalance (EQCM) and the formation of thin films by an automated flow deposition system. The formation and characterization of II-VI, Cd and Hg compounds as well as IV-VI, Pb based compounds by EC-ALE using an automated flow deposition system is the subject of this dissertation.

The EC-ALE deposition programs were developed by performing cyclic voltammetry studies using a TLE as indicated by previous work in this group [12-15]. Gregory investigated

the formation of CdTe by upd with a TLE on Cu, Au and Pt electrodes [12]; and subsequently reported conditions of forming CdTe by EC-ALE using a TLE [16]. The formation of films over 10 cycles proved tedious for TLE work, prompting the development of an automated flow deposition reported in previous articles [17]. Colletti [17] noted that major problems with the flow deposition system used then were uncompensated resistance ( $R_u$ ) and irregular solution flow, resulting in irreproducibility of the thin films formed. The formation of CdTe, CdSe and CdS by EC-ALE using a modified H-cell was reported by Colletti [17]. The problems with irreproducibility of the films were encountered. Progress was made in the flow cell design used and on the exclusion of oxygen by containing the pumps and valves in a N<sub>2</sub> purged Plexiglas box [18]. The new cell design showed reproducibility of the thin film growth, with the formation of InAs [19].

Electrochemical atomic-layer epitaxy (EC-ALE), the electrochemical analog of atomic layer epitaxy (ALE), continues to be developed in this laboratory and others, for the formation of thin films. EC-ALE makes use of underpotential deposition (upd) to electrodeposit single atomic monolayers of the elements making up a compound semiconductor. Upd is a well-documented phenomenon in which one element deposits onto another element at a potential prior to (under) that necessary to deposit the element onto itself. The resulting deposit is limited to an atomic monolayer. This is due to the surface limited nature of upd, which results in a structure that is independent of mass-transport. Electrochemical atomic-layer epitaxy (EC-ALE) is an alternative method for nanostructure fabrication. The main advantage EC-ALE has over MBE (Molecular Beam Epitaxy) and MOCVD (Metallo-Organic Chemical Vapor Deposition) is its ability to operate at ambient temperature and pressure conditions. This avoids problems with heat-induced interdiffusion of species. Also, EC-ALE is orthogonal to conventional methods, such as MBE

and MOCVD, possibly allowing new discoveries. In addition, the thickness of deposits is easily controlled. It is a simply matter of programming the number of EC-ALE cycles carried out [1]. Deposition of CdSe by EC-ALE will be discussed in Chapter 2, where it will be shown how the deposition cycles was improved by using a new flow cell design, with simpler solution compositions. The formation of HgSe and initial studies on the formation of HgTe by EC-ALE will be presented in Chapters 3 and 5 respectively. Hg UPD studies and electrodeposition dynamics have been reported for different substrates and electrolytes [20-23]. On the other hand, Hg chalcogenides have been scarcely investigated due to mercury toxicity [24]. The formation of HgSe has been done mostly by MBE [25] and lately by chemical bath deposition [24, 26].

HgTe has been formed by ALE [27], flash evaporation [28] and by conversion of HgO to HgTe at room temperature [29]. The studies of HgTe/CdTe superlattices [30-34] grown by chemical beam epitaxy [35], MBE [36] and wet chemical synthesis [37] for making infrared materials [38] have been reported.

The successful formation of CdSe and HgSe led to attempts to form a superlattice: CdSe/HgSe which will be discussed in Chapter 4. In that work, however, no evidence of a superlattice was obtained, leading to the conclusion that an alloy was formed instead. HgSe/CdSe heterostructures grown by MBE [39] and a quantum dot quantum well structure (CdSe/HgSe/CdSe) for quantum confinement studies [40] were reported. The electrochemical formation of CdSe/HgSe has not been studied to a large extent.

Pb chalcogenides reported in this dissertation include PbSe, which was modeled for quantum confinement, and PbTe/PbSe nanostructures, studied for the effects induced by changing the thickness of individual layers in the alternated deposition of PbTe and PbSe.

The nanostructures, heterostructures and thin films grown by EC-ALE were characterized for crystal structure and morphology, respectively by: X-ray diffraction (XRD) and Atomic Force Microscopy (AFM). Electron Probe Microanalysis (EPMA) was used to determine the stoichiometry, with deposit thicknesses measured by Ellipsometry. The bandgaps were determined by either Ultraviolet spectroscopy (UV-VIS), Photoconductivity or absorption (FTIR) measurements, with the exception of CdSe, where all these techniques were used.

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## CHAPTER 2

### DEPOSITION OF CDSE BY EC-ALE $^{\rm 1}$

<sup>&</sup>lt;sup>1</sup> M. K. Mathe, B. H. Flowers. Jr., L. Pham, S. M. Cox, U. Happek and J. L Stickney. to be submitted to *Chemistry* of Materials

#### 2.1 ABSTRACT

The optimization of a CdSe thin film deposition program using electrochemical atomic layer epitaxy (EC-ALE) is reported. EC-ALE exploits the use of surface limited reactions, underpotential deposition (upd), to deposit thin films one layer at a time on Au substrates. CdSe thin films were formed using an automated flow deposition system, by alternately depositing Se and Cd, forming a monolayer of a compound, each cycle. Deposits of 200 cycles were formed at different potentials. Cyclic voltammograms were used to establish a range of potentials that can be used to deposit CdSe thin films. Electron probe microanalysis (EPMA) of the deposits gave a stoichiometric ratio between 1.01 and 1.13, Cd/Se. X-ray diffraction patterns indicated the deposits as having the zinc blende structure with a preferred (111) orientation. The thickness of the deposits studied by AFM showed that good deposits formed on substrates with terraces of 200 – 600 nm. The bandgap of the deposits was determined by UV-VIS, photoconductivity and FTIR, and all suggested a value of 1.74 eV.

Keywords: CdSe, EC-ALE, Electrodeposition, upd, pH, concentration, monolayer, Ellipsometer, EPMA, XRD, zinc blende, UV-VIS, Photoconductivity, FTIR, bandgap

#### 2.2 INTRODUCTION

CdSe thin films have been formed using a number of methods, including molecular beam epitaxy (MBE), chemical vapor deposition (CVD), and evaporation and sputtering. These methods are generally performed in vacuum and are thermal methods. Electrochemical methods used for the formation of thin film semiconductor compounds include electrodeposition [1], codeposition[1-7] and precipitation [8]. One of the promising electrochemical methods presently

used by this lab and others is Electrochemical Atomic Layer Epitaxy (EC-ALE). EC-ALE is the electrochemical analog of atomic layer epitaxy (ALE), and makes use of underpotential deposition (upd) to electrodeposit single atomic monolayers of the elements making up a compound semiconductor. Upd is a well-documented phenomenon in which one element deposits onto another element at a potential prior to (under) that necessary to deposit the element onto itself. The resulting deposit is limited to an atomic layer. This is due to the surface limited nature of upd, which results in a structure that is independent of mass-transport. Several thin film semiconductor compounds were formed using this method [9-12]. Other groups are presently using EC-ALE to form compounds.

Earlier CdSe studies[9, 10] were performed with two blank solutions and different pHs for the precursor elements, Cd and Se. Problems encountered such as uncompensated resistance (R<sub>u</sub>), bubbles and edge effects prevented reproducibility of deposits. The solutions had buffers in them as well.

This paper describes recent progress in deposition of thin films of CdSe. The present experiments were done to optimize and simplify the system. The optimization of the conditions refers to the potentials at which the compounds grown were stoichiometric; the XRD diffraction patterns showed only CdSe and Au peaks and bandgap measurements matched reported literature values. To simplify the deposition of CdSe, the use of buffers was eliminated; the same pH and concentrations were used with good success.

#### 2.3 EXPERIMENTAL

The deposition instrument consists of computer-controlled pumps, valves and a potentiostat, been described elsewhere[13-15]. Most deposits are vulnerable to traces of oxygen during deposition, so the pump heads, valves and tubing were confined inside a  $N_2$  – purged

Plexiglass box. The electrochemical cell consists of a thin-layer design to promote laminar flow [14]. The electrodes (ITO and Au substrates) are held apart by a thick gasket, which defines a rectangular opening where the deposition takes place. The ITO auxiliary is transparent, allowing the deposition process to be followed visually. The reference electrode, Ag/ AgCl/ 3M NaCl (Bioanalytical Systems, Inc., West Lafayette, IN) is positioned at the cavity outlet [14].

The following solutions were used in earlier studies for CdSe deposition: 5mM CdSO<sub>4</sub> with a pH of 5.7, buffered with 50mM CH<sub>3</sub>COONa.3H<sub>2</sub>O (J.T. Baker). The selenium solutions was 0.5 mM SeO<sub>2</sub> with a pH of 5.5, buffered with 50mM CH<sub>3</sub>COONa.3H<sub>2</sub>O (J.T. Baker). These solutions were subsequently simplified to a common pH of 5.0, a similar concentration of 0.5 mM and complete exclusion of the use of buffers. The supporting electrolyte for all the solutions was 0.5 M Na<sub>2</sub>SO<sub>4</sub>, also used as a rinse solution with a pH of 5.0. The water used to make all the solutions was supplied from a Nanopure water filtration system (Barnstead, Dubuque, IA) from the house distilled water system. The chemicals were reagent grade or better.

The potentials for both Se and Cd were stepped at equal increments over the first 30 cycles to a steady state point. Cadmium potentials ranged from -0.300 V to -0.550 V, while selenium potentials ranged from -0.300 V to -0.580 V (all potentials referenced to Ag/AgCl).

The deposits were inspected with a Jenavert microscope. Ellipsometric measurements were performed using a single wavelength Sentech SE 400 (Micro Photonics Inc., Allentown, PA). Electron probe microanalysis (EPMA) was run on a Joel 8600 scanning electron microprobe, with a wavelength dispersive spectrometer. Glancing angle X-ray diffraction patterns were acquired on a Scintag PAD V diffractometer equipped with a thin – film attachment using CuK $\alpha$ radiation, ( $\lambda = 1.5418$ Å). AFM studies were performed using a Nanoscope III (Digital Instruments, Santa Barbara, CA). Absorption measurements were performed using a UV-VIS spectrophotometer and FTIR (Bruker FTS-66v, Bruker Optics, Inc). CdSe films were stripped from the Au substrate for photoconductivity measurements. Sample preparation involved forming a mask of epoxy over the deposit, and then prying the block off with the deposit, leaving the Au substrate. The conductivity was measured as a function of wavelength. A potential was applied across the film and the current measured as a function of the incident photon wavelength. The scan was from 1100 to 400 nm, and used a Cary 14 spectrophotometer. The ac component of the current was measured with a Stanford Research System SR830 lock-in amplifier. The sample was placed in a cryostat and cooled with liquid helium for the 16 K measurements.

### 2.4 RESULTS AND DISCUSSION

The formation of CdSe by EC-ALE has been previously reported [10]. In that study, CdSe thin films were formed using two different cycle chemistries. The first studies were performed using a cycle with a stripping step, that is, after deposition of Se at -0.6 V, a reduction in blank electrolyte, -0.8 V, was used to remove any extra Se. Cd was then deposited at -0.55 V [10]. Deposits formed were Se rich and fraught with reproducibility problems. The deposits showed a characteristic red color, consistent with too much Se, possibly the result of Se conproportionation [16].

Se deposition has been shown to be sensitive to pH and concentration changes [17, 18]. To take advantage of this, the pH of the Se solution was changed to 9.2. A new cycle was subsequently developed, where Cd and Se were both deposited reductively, with no stripping step. This new cycle deposited Cd at -0.6 V and Se at -0.9 V. CdSe deposits were again formed, this time with better stoichiometry, but still showing problems with reproducibility.

In the studies presented here concerning the growth of CdSe, the cycle involved pH 9.2 Se solutions and pH 5.7 Cd solutions, buffered respectively with sodium borate (Se) and sodium acetate (Cd). Again, reproducibility was a problem. It appeared that mixing of the basic Se solution with the Cd solution resulted in precipitation of Cd (OH)<sub>2</sub>, which was interfering with flow through the cell. It was then decided to use a less basic Se solution, to avoid the problem of hydroxide formation. Subsequently, deposits were formed using pH 5.5, an acetate buffer, for both Cd and Se

Cyclic voltammograms for both the  $Cd^{2+}$  and HSeO<sub>3</sub><sup>-</sup> solutions, used to form CdSe, are shown in Fig. 2.1. In the initial development of an EC-ALE cycle for CdSe, a potential of -0.2 V was suggested for both Cd upd (Fig.2.1.1) and Se upd (Fig. 2.1.2). It is probable that more negative potentials could have been used for the deposition of both elements, but complications with the formation of an alloy of Cd with the Au surface at potentials between -0.5 and -0.8V, suggested the more positive potential. Basically, for the first few cycles at least, the Cd deposition potential should be held above -0.5 V to avoid the possibility of an alloy disrupting the surface morphology [19]. It is presently believed in this group, that problems with alloy formation are limited to the first one or two cycles, at which point the growing compound thin film prevents further alloy formation, and more negative deposition potentials can be used, as long as bulk Cd is avoided (negative of -0.8 V).

The cycle for Se deposition on Au showed a series of broad peaks, prior to what looks like bulk deposition, suggesting surface limited reactions. Studies have shown, however, that the total Se deposited in the series of broad peaks is about five times more than needed to form a monolayer of CdSe [20]. Previous work suggests that after Se upd on Au, a couple more atomic layers of Se are deposited in a surface limited reaction, prior to what could be called bulk Se deposition. The nature of this surface limited reaction is still in question. Cycles for a number of compounds, grown with EC-ALE, have shown that the potentials used to form the first monolayers of a compound are insufficient to form full monolayers after the first few cycles. That is, from coulometry, the first cycle produces a compound monolayer, but subsequent cycles produce only a fraction thereof. The solution has been to adjust the potentials after each of the first 10–30 cycles [15, 21, 22]. The need for changes in the deposition potentials, after the first steps, is obvious, given that they represent upd on the Au substrate. Presently, it appears that the electronic structure of the deposit is influenced by the substrate for up to 30 cycles, thus accounting for the need to slowly change the potential as the deposit progresses. The potentials used progress to what we refer to as the steady state potentials, at which point the same potentials can be used for all subsequent cycles. As noted, the first few being different because of the substrate, makes sense. However, the reason that it can take 30 cycles is not yet clear. The flexibility of the LabView based deposition program, allows for adjustment of the deposition potentials with each cycle, in any functional form. Linear ramps with the number of cycles have been studied, as well as exponential. The steady state potentials are then maintained for all subsequent cycles. Presently linear and exponential steps were used, for both the Cd and Se deposition potentials, over the first 30 cycles, maintaining about a monolayer of deposition per cycle. The deposition cycle (Fig. 2.2) for the growth of CdSe consisted of a 2 second fill step for Se at -0.3 V, followed by 15 seconds of deposition, with no solution flow. The cell was then rinsed with a blank solution for 3 seconds and filled for 2 seconds with Cd, after which the solution was held for 15 seconds, during deposition at -0.3 V. Finally, the Cd solution was flushed with the blank solution for 3 sec. This cycle forms a monolayer of CdSe. As noted above,



Figure. 2.1.1: Cyclic voltammograms of Cd<sup>2+</sup> [0.5 mM], pH 5.7



Figure 2.1.2: Cyclic voltammograms of HSeO3<sup>-</sup> [0.5 mM], pH 5.7

however, the amounts deposited drops off with succeeding cycles so the deposition potentials were adjusted over the first 30 cycles until steady state potentials of -0.58 V for Se and -0.55 V for Cd were reached. In general, 200 cycle deposits were formed in this study. This thickness allowed analysis using XRD, ellipsometry, and EPMA. Overall, the Cd and Se coverages per cycle, at the steady state potentials, averaged 0.48 ML for Se and 0.45 ML for Cd, as determined from integration of current time traces such as those shown in Fig. 2.3. Finally, the solutions were simplified further, excluding the use of buffers, using a common pH (5.0) solution with no buffer, and 0.5 mM for both solutions. Starting deposition potentials of -0.3 V were used for both Se and Cd, as well, with final potentials of -0.58 V for Se and -0.55 V for Cd. These deposition conditions resulted in deposit with good stoichiometry, close to the theoretical thickness (one compound ML/cycle) and a room temperature bandgap of 1.74 eV, in agreement with



Figure 2.2: CdSe deposition cycle: The fill steps are done with solution flowing and the deposition steps are without solution flow.

literature values (Table 2.1). As ellipsometry is only accurate for smooth surfaces [23], rough deposit were difficult to measure with any degree of certainty via ellipsometry. An estimate of the quality of the deposits was obtained using a 1000X optical metallographic microscope. Some deposits were clearly rough, even to the eye, as they were not reflective, and with the microscope, particle (3D) growth was clearly evident. Such deposits were generally obtained if the potentials were pushed into bulk deposition, below -0.75 V. In such cases, ellipsometric measurements were fallacious.

EPMA was used to follow CdSe deposit stoichiometry. The EPMA Cd/Se ratio data, for a series of deposits made on different days using slightly differing conditions, ranged from 0.93 to 1.06 and this data is presented in Table 2.1. In general, the deposits were a couple percent rich in Cd (Table 2.1). Microscopic observations showed that deposits were uniform and conformal on the substrates. Color changes were readily observed after 30 cycles, a brown color was evident, which changed to a brown-purple by the 88<sup>th</sup> cycle and to deep purple after 132 cycles. The final color for 200 cycle deposits was a bluish green. These color changes were observed at the edges of a deposit by optical microscopy. Deposit edges display a continuum of thickness, a rainbow of colors, from no deposit to the full thickness. The roughness of a deposit was, first of all, a function of the quality of the substrate. However, the deposit morphology was also dependent on the applied steady state potential. Plots of deposit thickness (as measured by ellipsometry) vs. steady state deposition potentials, have been used to help optimize the deposition parameters, and are presented in Fig. 2.4 for Cd and Se. 200 cycle thick deposits were used in Figure 2.4, for the study of the thickness as a function of potential. In Figure 2.4A, the steady state potential for Cd was held at -0.65 V while that for Se was varied. In Figure 2.4B, the steady state potential for Se was held at -0.68 V, while that for Cd was varied. A plateau in coverage as a function of potential is expected, in a potential range where the coverage is controlled by a surface limited reaction, rather than potential.



Figure 2.3: Current time traces for Cd and Se deposition. The traces are used to calculate the amounts of Cd and Se deposited for respective cycles.

To optimize deposition conditions, the potential should be selected from the middle of this plateau region. Ideally 200 cycles results in a 70 nm thick deposit. In Figure 2.4A, there is no real clear cut plateau, however, the deposit formed at -0.58 V is just below the desired thickness, while that at -0.68 V is just above the 70 nm anticipated. At potentials above -0.68 V, the coverages with ellipsometry look alright, but examination using the optical microscope showed them to be roughened, making ellipsometric data useless. EPMA studies, however,



Figure 2.5: 2.5A at the top is for Cd study and 2.5B (bottom), Se study

Sample	Deposition Potentials (V)	EPMA (Cd/Se)	Thickness (nm)	E <sub>g</sub> (eV)
CdSe3/06/03	Cd: -0.300 V to -0.550 V; Se -0.300 V to -0.580 V	?	69.67	$1.740\pm0.018$
CdSe3/18/03	Cd: -0.300 V to -0.550 V; Se -0.300 V to -0.580 V	1.13	77.8	?
CdSe3/21/03	Cd: -0.300 V to -0.700 V; Se -0.300 V to -0.700 V	1.01	85.55	$1.718\pm0.026$
CdSe3/24/03	Cd: -0.300 V to -0.650 V; Se -0.300 V to -0.650 V	1.01	69.31	$1.725\pm0.025$
CdSe3/25/03	Cd: -0.300 V to -0.550 V; Se -0.300 V to -0.580 V	1.07	69.75	?
CdSe3/28/03-1	Cd: -0.300 V to -0.650 V; Se -0.300 V to -0.675 V	1.03	71.94	$1.717\pm0.015$
CdSe3/30/03	Cd: -0.300 V to -0.675 V; Se -0.300 V to -0.650 V	1.01	70.33	$1.701\pm0.017$
CdSe3/31/03	Cd: -0.300 V to -0.625 V; Se -0.300 V to -0.625 V	?	71.32	$1.719\pm0.007$

Table 2.1: Results of stoichiometry, thickness and bandgap measurements for deposits grown under different conditions

suggest a much higher coverage, consistent with the roughening observed with the microscope. The problem is that at these negative potentials, some bulk deposition occurs, and layer by layer growth is no longer possible. At potentials positive of -0.58 V, the coverage drops dramatically, as less then a ML/cycle is deposited, until -0.4 V, where essentially no deposit is formed. XRD has been used to evaluate the crystal structure of the CdSe deposit. The diffraction geometry, as noted in the experimental section, involves a constant incident angle on the surface, usually 1.1° off parallel with the deposit, and scanning the detector through  $2\theta$ . The detector is equipped with Soller slits to limit detection of scattered X-ray, and accentuate the diffracted photons. The diffraction pattern in Fig. 2.5 consisted of peaks characteristic of zinc blende CdSe, with peaks at  $2\theta = 25$ , 42, and 49 degrees, matching the card file [JCPDS 19-0191]. In addition, peaks for the Au substrate, are present at 38, 44 and 64 degrees. Ratios of the Au to CdSe peaks are a function of the angle of incidence of the X-rays, with the Au peaks growing and the CdSe shrinking as the angle of incidence increases. No peaks other than those for Au or CdSe were observed, that is, there were no peaks for elemental Cd or Se. A strong (111) habit is evident for the Au substrate. The CdSe shows some preferential (111) habit. The peaks for the CdSe were broader then have
been observed for other compounds formed by EC-ALE, and at present it is not clear why. Calculations based on a 2:3 lattice match, two surface unit cells for the CdSe matching up with 3 surface unit cells for the Au, have suggested less then a 1% mismatch. However, this matching does not appear to be controlling the CdSe deposit, as peak ratios resemble more that of a polycrystalline deposit, than the expected (111) oriented deposit. Studies using single crystal Au substrates are planned.

The effect on morphology of the substrates was studied by AFM, in tapping mode. The images of the Au substrates and corresponding CdSe deposits (5X5  $\mu$ m) are shown in Figs. 2.6 (CdSe3/06/03) and 2.8 (CdSe3/28/03-1). The substrates differed, in that the first Fig. 2.6 looked dull to the eye. It had been through a more prolonged annealing process, and as can be seen in the image, consisted of fairly large angular terraces, 200 – 600 nm. In contrast, shiny substrates with the familiar gold color (Fig. 2.7), exhibited a rough or, less crystalline, morphology with the AFM. CdSe3/06/03 showed comparable features to the substrate indicative of good conformality, and layer by layer growth. The quality of the deposit is shown in Table 2.1 (CdSe3/06/03) by a bandgap of 1.74 eV, corresponding to the room temperature bulk value [24]. The micrograph of CdSe3/28/03-1 (Fig. 2.8) shows crystallites which implies some possible 3D growth, corresponding to bulk deposition potentials indicated in Table 2.1.

FTIR measurements of 200 cycles EC – ALE deposited CdSe thin films, were performed to determine the bandgaps and thus the deposit quality. Bandgaps for deposit formed with different conditions are presented in Table 2.1. Bandgap values that could not be determined are shown by a question mark. The lack of absorption in samples CdSe3/18/03 and CdSe3/25/03 needs further investigation since these samples were fairly stoichoimetric with reasonable thickness (Table 2.1), also they were formed using potentials like those used in sample

CdSe3/06/03. Substrate treatment and morphology are likely explanations for lack of absorption. The room temperature absorption measurements are presented as plots of  $\alpha^2$  vs. *hv*, shown in Fig. 2.8 for both CdSe3/06/03 and CdSe3/28/03-1. The bandgap values were determined by linear extrapolation to the X-axis (*hv*) from the straight part of the curve. CdSe thin films were deposited on indium tin oxide (ITO) coated glass substrates for transmission measurements in a UV-VIS spectrophotometer.



Figure 2.5: XRD diffraction pattern of EC-ALE deposited CdSe



05121322.001 CdSe 3/6/03 200cy GOLDSUB



Figure 2.6: CdSe30603 AFM micrograph. At the top is the micrograph of the Au substrate, and bottom micrograph is the deposit morphology



Figure 2.7: CdSe32803/1 AFM micrograph at the top is the micrograph of the Au substrate and bottom micrograph is the deposit morphology

Transmission measurements for both the clean ITO and ITO with deposits were recorded in a wavelength range of 300 to 900 nm. The measurements were used to give a plot of  $(\alpha hv)^2$ 

vs. hv shown in Fig. 2.9, from which the bandgap of 1.74 eV was determined by drawing a straight line to the X-axis.

CdSe films were stripped from the Au substrate for photoconductivity measurements. Two scans were done on the film at each temperature. The normalized raw data presented in Fig. 2.10 was used to determine the deposit bandgap. Currents were assumed proportional to the absorption coefficient. Currents were plotted against absorption measurements for a direct bandgap semiconductor; the linear part of the square of the absorption coefficient versus the energy function was extrapolated to obtain the bandgap onset from Fig. 2.11. At room temperature, the band gap for the film was about 1.65 eV and 1.75 eV at low 16 K.



Figure 2.8: Absorption spectra used in bandgap determination. Top figure is for CdSe3/06/03 and the bottom figure is CdSe3/28/031



Figure 2.9: UV-VIS bandgap determination of CdSe deposited on ITO



Figure 2.10 A: Photocurrents for a CdSe deposit



Figure 2.11: Bandgap spectra of a CdSe measured by photoconductivity

#### 2.5 CONCLUSIONS

The deposition of CdSe thin films by EC-ALE has been reported. The deposition conditions were optimized by changing solution compositions from those used in earlier studies by Colletti, et al. [10]. By eliminating the use of buffer and using similar concentration (0.5 mM) and a pH 5.0 for cadmium and selenium, reproducible, good quality deposit were formed. The deposits formed were zinc blende (cubic) with a dominant (111) orientation. Substrate and deposit AFM micrographs correlated well with FITR bandgap measurements, establishing that deposit quality depends on the substrate morphology. The bandgap of CdSe thin films measured by FTIR, UV-VIS and photoconductivity gave a room temperate value of 1.74 eV, corresponding to the bulk literature value.

## 2.6 ACKNOWLEDGEMENTS

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# CHAPTER 3

# FORMATION OF THIN FILMS OF HGSE USING ELECTROCHEMICAL ATOMIC LAYER

EPITAXY<sup>2</sup>

<sup>&</sup>lt;sup>2</sup> M. K. Mathe, S. M. Cox, U. Happek and J. L. Stickney. to be submitted to *The Journal of Electroanalytical Chemistry*.

#### 3.1 ABSTRACT

Growth of HgSe using electrochemical atomic-layer epitaxy (EC-ALE) is reported. EC-ALE takes advantage of underpotential deposition (upd), deposition of a surface limited amount (a monolayer or less) of an element at a potential less than that needed for bulk deposition, to form a thin film of a compound--one atomic layer at a time. HgSe thin films were formed on gold substrates using Hg<sup>+2</sup> complexed with ethylenediaminetetraacetic acid (EDTA) and HSeO<sub>3</sub><sup>-1</sup> ions. XRD analysis showed a zinc blende structure for the deposits, with a preferential (111) texture, and an average grain size of 425Å. Electron Probe Microscope Analysis (EPMA) showed stoichiometric deposits but a few percent rich in selenium. Fourier Transform Infrared spectroscopy (FTIR) absorption measurements showed two bandgaps of 0.42 eV and 0.88 eV. Keywords: HgSe, EC-ALE, upd, Electrodeposition, XRD, EPMA, FTIR, bandgap

#### 3.2 INTRODUCTION

Cadmium and zinc chalcogenides have been extensively studied, mainly for their applications in optoelectronic devices. HgSe has possible uses in optoelectronic applications, IR detectors, IR emitter, tunable lasers and thermoelectric coolers[1]. The electrodeposition of mercury chalcogenides has been little studied, due to the high formal potential for Hg, compared to the chalcogenides, and its toxicity[2]. Formation of HgSe by MBE [3], chemical bath deposition [1, 2, 4] and the Cold Travelling Heater Method (CTHM) [4, 5] has been reported. For the formation of HgSe by MBE, GaAs substrates were used [3], while glass slides were used for chemical bath deposition [1], as well as SnO<sub>2</sub> coated glass slides [5] and transparent polyester sheets[6]. Hg upd studies and electrodeposition dynamics have been reported for different substrates and electrolytes [7-9]. The nature of HgSe as a metal or semiconductor continues to be debated as shown by Gawlik et al. [10], who determined its direct bandgap of 0.42 eV suggesting a semiconductor. HgSe Fourier transform spectroscopy band structure studied by von Truchse $\beta$  et al. [11], concluded that it was a semimetal with an inverted structure, and a bulk gap of -0.274 eV. Other studies of the HgSe bandgap reported values of 1.42 eV [4], 2.50 eV and recently a direct bandgap of 0.81 eV and an indirect bandgap of 0.45 eV were also shown [1].

Electrochemical atomic-layer epitaxy (EC-ALE) is an approach to the electrodeposition of thin-films of compound semiconductors. It is the electrochemical analog of atomic layer epitaxy (ALE) or atomic layer deposition (ALD), both of which are gas or vacuum phase method for the formation of compounds an atomic layer at a time using surface limited reactions. Electrochemical surface limited reactions are generally called underpotential deposition (upd). Upd is used in EC-ALE to achieve monolayer by monolayer growth. Upd is the deposition of one element on a second at a potential prior to that needed to deposit the bulk element.

Many II-VI and a few III-V compounds have been formed by EC-ALE. II-VI films such as CdSe, CdS, and CdTe have been successfully formed by chemical methods [12-22]. In addition, deposition of the III-V compounds InAs [23] and InSb have been formed, along with initial studies of GaAs [24] and GaSb deposition. Recently, IV-VI compounds such as PbSe and PbTe and their superlattices (PbSe/PbTe) [25-27] were formed using EC-ALE.

We report for the first time, the formation of HgSe using EC-ALE. These deposits were formed on the Au on glass substrates. The films were characterized using X-ray diffraction (XRD), Electron Probe Microscope Analysis (EPMA), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Fourier Transform Infrared spectroscopy (FTIR). XRD diffraction patterns indicated the films to have a zinc blende structure. EPMA results indicated the films as stoichiometric, with less than 5% excess selenium. Infrared absorption measurements showed direct and indirect bandgaps of 0.42 eV and 0.88 eV.

#### 3.3 EXPERIMENTAL

The deposition instrument for the formation of thin films has been previously described [23, 28, 29]. The pump heads, valves and tubing were confined inside a  $N_2$  – purged Plexiglass box to limit the amount of oxygen present, which affects the deposit quality. The electrochemical cell consisted of a thin-layer design to promote laminar flow. The electrodes (ITO auxiliary and Au substrate) were held apart by a silicon rubber gasket, which defined a rectangular opening where deposition took place. The ITO auxiliary is transparent, allowing the deposition process to be followed visually. The reference electrode, Ag/AgCl (3M NaCl) (Bioanalytical Systems, Inc., West Lafayette, IN) is positioned at the cavity outlet [29].

The solutions used included 0.2 mM HgCl<sub>2</sub>, pH 2.00, complexed with 10 mM ethylenediaminetetraacetic acid (EDTA). The concentration of SeO<sub>2</sub> solution was 0.25 mM, pH 3. A 0.5 M NaSO<sub>4</sub>, pH 4.0 blank solution was used as well. Solution pH was adjusted with H<sub>2</sub>SO<sub>4</sub>. The supporting electrolyte was 0.5 M NaSO<sub>4</sub>. The water used to make all the solutions was supplied from a Nanopure water filtration system (Barnstead, Dubuque, IA) hooked to the house distilled water system. The chemicals were reagent grade or better. Microscope glass slides with a 3 nm Ti adhesion layer and 600 nm of Au were used as substrates. The slides were etched in a 15% HF for 60 seconds and rinsed

with ultra pure water prior to insertion in the vapor deposition chamber. The substrates were annealed at 400 °C for 12 hrs before deposition [26].

Film growth on the Au substrates was performed as follows: The cell was filled by a pump from a reservoir containing an electrolyte solution of a precursor to the element of interest (Se). The solution was held for 15 seconds for the deposition, and then flushed from the cell with the blank. This was followed by filling the cell with the second elemental precursor (Hg), and holding for deposition. The cycle was then completed by flushing the second elemental precursor from the cell with the blank, and refilling with the first. This cycle, ideally, results in the deposition of one monolayer of the compound. The thickness of a deposit is determined by the number of times the cycle is performed.

The deposits were inspected with a Jenavert microscope. Scanning Electron Microscope was used to study the morphology of the deposit. The thickness was measured using a single wavelength Ellipsometer (SE 400). Glancing angle X-ray diffraction patterns were acquired on a PAD V diffractometer with CuK $\alpha$  radiation, ( $\lambda = 1.5418$ Å) equipped with a thin film attachment. Electron probe microanalysis (EPMA) was run on a Joel 8600 scanning electron microprobe, with a wavelength dispersive spectrometer. AFM studies were performed using a Nanoscope III (Digital Instruments, Santa Barbara, CA). Absorption measurements were performed in reflection mode, using a FTIR spectrophotometer.

#### 3.4 RESULTS AND DISCUSSION

The starting potentials for the deposition program were determined from the cyclic voltammograms of Hg and Se. Typical voltammograms for Hg and Se are shown in Figures 3.1 and 3.2 respectively. The Hg scan was started at 0.7 V in a cathodic direction and shows a

reductive deposition peak ( $C_{II}$ ) at 0.3 V (Figure 3.1), possibly some form of upd, and a peak which appears diffusion limited at 0.15 V, probably bulk deposition of  $Hg^{2+}$  to Hg. What is interesting is that bulk Hg deposition would be expected at 0.4 V. This suggests the deposition process is relatively irreversible. There are two other issues, one is that it is well known that Hg readily alloys with Au, to form an amalgam. In addition, previous work in this group suggest that prior to bulk deposition of Hg on Au, in thin layer electrochemical studies, where the amount of Hg<sup>2+</sup> in the solution is limited by the small volume of the solution in contact with the electrode (3µL/cm<sup>2</sup>) there are two reduction features which at first look like two upd peaks. However, using rinsing studies, after the first reduction peak, if the solution is exchanged for blank electrolyte and the scan direction is reversed, no evidence of deposited upd Hg in Fig. 3.3 was observed. This suggests that  $Hg^{2+}$  may be passing through a soluble intermediate, such as  $Hg_2^{2+}$ . However, analysis is impeded by the affinity of the Au surface for the Hg, and formation of an alloy. At present, the initial stages of Hg deposition on Au remain obscure. However, from Fig. 3.1 it does appear that the majority of Bulk Hg deposition can be avoided by using potentials positive of 0.25 V. The cathodic Se scan (Figure 3.2) was started at 0.4 V and showed initiation of reduction at 0.25 V, with a peak at 0.05 V. In addition, there are reduction features at -0.4, -0.55 and -0.7 V. The formal potential for Se is about 0.4V. From experience, it appears that by keeping the potential above -0.4 V, bulk Se deposition can be avoided. However, given a formal potential for Se deposition of 0.4, it is clear that classic upd does not exist. Even the peaks at 0.25 V deposit at an overpotential, but with the irreversibility of the Se process, it has been found that a surface limited like deposition can be obtained above -0.4 V [30-33]. Given the above discussions, potentials of 0.275 V for Hg (Fig.3.1) and -0.15 V Se (Fig 3.2) were chosen as starting potentials. The deposition cycle for the growth of HgSe consisted of a 2 second fill step

for Hg at 0.275 V, followed by 15 seconds of deposition with no solution flow. The cell was then rinsed out with a blank solution for 3 seconds and filled for 2 seconds with the Se solution, and held at -0.15V for 15 seconds for deposition.



Figure 3.1: Cyclic voltammogram of 0.2 mM Hg<sup>2+</sup>, pH 2.0

Finally, the Se solution was flushed from the cell with 4 seconds of the blank. The intent is for each cycle to result in the deposition of a HgSe compound monolayer, with the deposit thickness increasing linearly with the number of cycles. The deposition current time traces indicated formation of a compound ML each cycle, for the first 10 cycles, if the potentials were adjusted slightly over the first 10 cycles, to better optimize the deposit. The reasons that such potential

shifts are need for the first 10 cycles are not clear, but appear to result from an influence of the Au substrate over the deposition chemistry. As the deposit gets thicker, the first 10 cycles, the influence of the Au substrate goes away, and steady state conditions are reached. The steady state potentials can be used for all subsequent cycles, 0.15 V for Hg and -0.18 V for Se, for the deposits reported here.



Figure 3.2: Cyclic voltammogram of 0.25 mM Se<sup>2-</sup>, pH 3.0



Figure 3.3: Hg blank rinse study on TLE

The principle of EC-ALE is that upd is used to promote 2D or layer by layer growth. STM studies of Hg deposition on Au suggest that UPD does occur [1, 4, 6, 34-36], while it only deposits on HOPG at an overpotential [9]. Current traces observed in the formation of HgSe indicated that Hg deposition occurs in a upd like surface limited reaction. While from current time traces, Se deposition appears to have two components, a fast surface limited deposition, followed by a slow back ground deposition, which appears to be bulk deposition. To try and better optimize film quality, a series of deposits were formed using different steady state potentials. Deposit quality was monitored using EPMA for stoichiometry (Table 3.1), and XRD

for structure (Figures 3.4 (a –d). Coverages at the steady state potentials averaged 0.37 ML for Hg and 0.52 ML for Se relative to one atom per Au (111) surface atom being equal to 1.0 ML, as measured using coulometry. Deposits formed were Se rich as shown in Table 3.1 and as suggested by coulometry. Ellipsometric thickness measurements indicated the linear increase in thickness with the number of cycles performed, as expected (Fig. 3.5), indicating that the thickness of the deposits was a factor of the number of cycles and not applied potential.

The XRD patterns for 100 and 200 cycles HgSe deposits grown at different steady state potentials are shown in Figures 3.4 (a) – (d). From the diffraction patterns, peaks corresponding to (111), (200), (220), (311), (222), (400) and (331) planes of HgSe are shown, matching the JCPDS 8-469 card and indicating a zinc blende deposit.

Sample	# of cycles	Th (nm)	Se/Hg
HgSe4/27/03	156 cycles	55.37	4.10
HgSe5/15/03	100 cycles	17.84	0.73
HgSe6/11/032	50 cycles	15.64	1.11
HgSe6/16/03	50 cycles	24.95	1.13
HgSe6/22/03	65 cycles	18.76	1.39
HgSe6/23/03	100 cycles	56.65	1.54
HgSe6/24/03	100 cycles	48.41	1.68
HgSe6/4/03	100 cycles	33.03	1.02
HgSe6/5/03	100 cycles	45.74	0.99
HgSe6/5/03	50 cycles	11.65	0.90
HgSe6/8/03	50 cycles	26.50	0.89
HgSe6/9//03	100 cycles	34.51	0.99
HgSe6/9/03	200 cycles	66.72	0.99
HgSe6/9032	200 cycles	59.40	0.97

Table 3.1: Thickness and stoichiometry data of HgSe deposits



Figure 3.4 A: XRD diffraction pattern for HgSe 50803, showing the present HgSe peaks. The elemental peaks for Hg and Se were not present.



Figure 3.4 B: XRD diffraction pattern of HgSe 69033.



Figure 3.4 C: XRD diffraction pattern of HgSe 69032.



Figure 3.4D: XRD diffraction pattern of HgSe 50603. The diffraction pattern shows a peak broadening on the HgSe (111) and a spread (200) peak.

Only peaks for HgSe and the Au substrate were evident in the XRD, no elemental peaks for Hg or Se were evident. The peak pattern suggested a polycrystalline deposit, but all deposits showed a pronounced (111) peak. Substrate properties continue to be investigated, as one of the factors in understanding why the (111) peak is pronounced in the HgSe deposit.

AFM micrographs of a 100 cycle deposit and the gold substrate are shown in figures 3.6 (a) and (b). The substrate scan size is 5 x 5 $\mu$ m shows and 200 to 600 nm wide plateaus. The deposit micrograph showed a lack of conformity with the substrate, suggesting the possibility of 3D growth, not 2D, required for epitaxy. SEM micrographs of HgSe with magnifications of 10K

X and 20K X are shown in Figure 3.7, where 200 nm particles, composed of smaller particles, were observed, and agree with the AFM micrographs in Fig. 3.6. The Scherrer equation (1) was used to calculate grain size.

$$D = \frac{K\lambda}{B\cos\theta} \tag{1}$$

where K = 0.9,  $\lambda$  is the wavelength of 1.5418 Å. B is the FWHM in radians and  $\theta$  the Braggs diffraction angles [1]. An average grain size of 42.5 nm was determined for the deposits. Note however that the films were only about 70 nm thick.

Room temperature absorption measurements of HgSe deposits exhibited an absorption range of 6000 -1500 cm<sup>-1</sup> as shown in Fig. 3.8 The bandgap was determined from a plot of  $\alpha^2$  vs. hv using equation (2)

$$\alpha$$
 (hv) = A (hv – E<sub>g</sub>)<sup>1/2</sup> .....(2)

where  $\alpha$  (hv) is the absorption coefficient, hv is the photon energy, A is the proportionality constant, and E<sub>g</sub> is the direct energy gap. Figure 3.9 shows a plot of the square of the absorption data for the 100 cycle deposit. The absorption measurements showed a direct band gap 0.42 eV and an indirect band gap 0.88 eV. The values are in good agreement with literature values of 0.45 eV and 0.81 eV [1].



Figure 3.5: Thickness plot of different number of cycles of HgSe deposits





Figure 3.6: The top micrograph (A) shows the Au substrate and (B) at the bottom shows the HgSe deposit, with small crystallites also observe in Fig. 3.7 below.



Figure 3.7: Top micrograph (A) was taken at a 10K magnification and (B) at the bottom was taken at 20K. Large particles are observed indicative of a possible 3D growth.



Figure 3.8: HgSe absorption spectra with a dip around 1500 cm<sup>-1</sup>.



Figure 3.9: Plot for the indirect and direct bandgap determination using equation (2).

### 3.5 CONCLUSIONS

The formation of HgSe thin films by EC-ALE has been shown for the first time. The growth conditions, from current time traces, compliment the EPMA results, showing that deposits were selenium rich at positive Se potentials. The deposition mechanism of HgSe will be the subject of future STM and EQCM studies. Optimized conditions for the growth of HgSe thin films will be fortuitous in the formation of HgSe/CdSe and HgSe/PbSe superlattices. The XRD patterns have showed that the HgSe deposits are polycrystalline with a preferential (111) orientation. Bandgap measurements showed the existence of direct and indirect energy gaps of 0.42 eV and 0.88 eV, respectively.

### 3.6 ACKNOWLEDGEMENTS

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# CHAPTER 4

# EC-ALE DEPOSITION OF CDSE/HGSE THIN FILMS<sup>3</sup>

<sup>&</sup>lt;sup>3</sup> M. K. Mathe, S. M. Cox, U. Happek and J. L. Stickney to be submitted to *Applied Surface Science*.

### 4.1 ABSTRACT

Room temperature electrodeposition of CdSe/HgSe thin films by electrochemical atomic layer epitaxy (EC-ALE) is reported. CdSe/HgSe thin films of 40 and 50 periods were formed after deposition of a 30 cycle CdSe buffer layer, by alternate deposition of 4 cycles of HgSe and 4 cycles CdSe at constant potentials. The deposits were formed on Au substrates, which showed a preferential (111) orientation. The deposits had a zinc blende crystal structure with a pronounced (111) orientation in the diffraction patterns, determined by X-ray diffraction. The deposits were conformal to the substrates. A room temperature direct energy gap of 0.66 eV was measured by FTIR.

*Keywords*: Electrodeposition; CdSe/HgSe thin films; X-ray diffraction; direct energy gap; gold substrates

#### 4.2 INTRODUCTION

HgTe/CdTe superlattices are the most highly and studied of the HgX/CdX systems [1-6]. The lattice constants of HgX and CdX are well matched, as suggested by the 0.08% lattice mismatch for CdSe/HgSe, [7] . Lattice-matched heterostructures, "Schottky barriers", form at the interface of the mercury – chalcogenide/ with the cadmium chalcogenides, and result in interesting optical properties [7]. HgSe/CdSe heterostructures grown by MBE [8] and hydrogen transport CVD [7], were studied by photoemission spectroscopy for conduction band discontinuities. HgSe/CdSe heterostructures have been expanded to a quantum dot quantum well structure (CdSe/HgSe/CdSe) for quantum confinement studies [9].

CdSe has been formed by several different electrochemical methods including, electrodeposition [10], codeposition [10-16] and precipitation [17]. However, few studies of the electrochemical formation of HgSe thin films have been reported [18-22].
A promising electrochemical method presently used by this laboratory and others, is Electrochemical Atomic Layer Epitaxy (EC-ALE). EC-ALE is the electrochemical analog of atomic layer epitaxy (ALE), and makes use of underpotential deposition (upd) to electrodeposit single atomic monolayers of the elements making up a compound semiconductor. Upd is a welldocumented phenomenon in which one-element deposits onto another element at a potential prior to (under) that necessary to deposit the element onto itself. The resulting deposit is limited to an atomic layer. This is due to the surface limited nature of upd, which results in a structure that is independent of mass-transport. Several thin film semiconductor compounds were formed using this method [23, 24-29]. Other groups are presently using EC-ALE to form compounds.

The formation of CdSe/HgSe thin films by EC-ALE is reported, for the first time. Characterization of these thin films was performed using a Jenavert Optical Microscope, Ellipsometer (SE 400), Electron Probe Microanalysis (EPMA), X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and Fourier Transform Infrared spectroscopy (FTIR) measurements. EPMA results indicated the films were stoichiometric, with a slight excess of mercury selenium. XRD diffraction pattern indicated the formation of zinc blende deposits, with a preferred (111) orientation. Infrared absorption measurements showed a direct energy gap of 0.66 eV.

#### 4.3 EXPERIMENTAL

The deposition system used in the formation of thin films by EC-ALE has been previously described [30-32]. A  $N_2$  – purged Plexiglass box was used to exclude oxygen from contact with the pump heads, valves and tubing. Oxygen exposure has been shown to decrease deposit thickness. The electrochemical cell consists of a thin-layer design, to promote laminar flow. The electrodes (ITO auxiliary and Au substrate) were held apart by a silicon rubber gasket, which defined a rectangular opening where the deposition took place. The thickness of the gasket used changed the cell volume, with a thick gasket gave rise to a 300  $\mu$ L volume. The ITO auxiliary was transparent, allowing the deposition process to be followed visually. The reference electrode, Ag/AgCl (3M NaCl) (Bioanalytical Systems, Inc., West Lafayette, IN) was positioned at the cavity outlet [32].

The water supplied from a Nanopure water filtration system (Barnstead, Dubuque, IA), the house distilled water system, was used to make all the solutions. The supporting electrolyte was vacuum-filtered 0.5M sodium sulfate (Fischer Chemicals), also used as a blank. Sulfuric acid (Fischer Chemicals) was used to adjust the pHs of all the solution used. Concentrations for both cadmium and selenium were 0.5mM and pH 5.0. Solutions were prepared from Cadmium sulfate and Selenium dioxide precursors of high purity (99.999%, supplied by Aldrich Chemicals). The HgCl<sub>2</sub> concentration was 0.2 mM, pH 2.0 and complexed with 10 mM ethylenediaminetetraacetic acid (EDTA). The SeO<sub>2</sub> concentration was 0.25 mM, pH 4.0. A pH 5.0 blank solution was used as well. All chemicals were reagent grade or better.

Gold substrates were used to deposit the CdSe/HgSe thin films. The Au substrates were microscope glass slides with a 3 nm Ti adhesion layer and 600 nm Au. The slides were initially etched in a 15% HF for 60 seconds and rinsed with ultra pure water prior to insertion in the vapor deposition chamber. The substrates were annealed at 400 °C for 12 hrs before deposition [28]. Substrates were cleaned in nitric acid and then annealed with a  $H_2$  flame to a dull orange color before making deposits.

CdSe/HgSe thin films were grown on 30 cycles of CdSe, the buffer layer. The buffer layer growth was performed as follows: The cell was filled using a pump, from a reservoir containing an electrolyte solution of a precursor to the element of interest (Se) for

2 seconds. The solution was held for 15 seconds for deposition, and then flushed from the cell with a 3 seconds blank rinse. This was followed by pumping in the second elemental precursor (Cd) for 2 seconds and holding for deposition for 15 seconds. This cycle should ideally result in the deposition of one monolayer of the compound, 1 ML. Following the deposition of the buffer layer, 4 cycle of HgSe were deposited alternately with 4 cycles of CdSe to form one period. Deposits of 40 and 50 periods were made.

The deposits were inspected with a Jenavert microscope. Glancing angle X-ray diffraction patterns were acquired on a Scintag PAD V diffractometer with CuK $\alpha$  radiation, ( $\lambda = 1.5418$ Å) equipped with a thin film attachment. Electron probe microanalysis studies were performed using a Joel JXA – 8600 superprobe. AFM studies were performed using a Nanoscope III (Digital Instruments, Santa Barbara, CA). Absorption measurements were performed in reflection mode, using an FTIR (Bruker FTS-66v, Bruker Optics, Inc.) spectrophotometer.

### 4.4 RESULTS AND DISCUSSION

Cyclic voltammograms for the formation of CdSe and HgSe have been previously reported [33, 34]. Reported here is the use of the deposition programs to form CdSe/HgSe thin films by EC-ALE. CdSe/HgSe thin films were formed on a 30 cycle CdSe buffer layer by alternately depositing 4 cycles of HgSe and then 4 cycles of CdSe, to form one period. The 8 cycle period was repeated 40 and 50 times to form thin films.

The CdSe/HgSe thin films were formed using steady state potentials, without ramping. The deposition cycle for the growth of CdSe consisted of a 2 second fill step for Se at -0.3 V, followed by a 15 seconds of deposition with no solution flow. The cell was then rinsed out with a blank solution for 3 seconds and filled for 2 seconds with Cd, after which the solution was held with no flow for 15 seconds for deposition at -0.3 V. Finally, the Cd solution was flushed from the cell with the blank solution. This cycle should form a monolayer of CdSe. The same cycle was used 30 times to form the buffer layer. The program used for the deposition of HgSe was performed similarly to that for CdSe, described above. The steady state potentials used to deposit HgSe were 0.15 V for Hg and -0.18 V for Se. The Cd coverages during deposition of the buffer layer decreased more than Se coverages, which stabilized at 0.2 ML per cycle after the 25<sup>th</sup> cycle. The ML coverages reported are relative to one atom per Au(111) surface, with an atom equal to 1.0 ML.

Cd coverages were lower than 0.2 ML per cycle, after the 4<sup>th</sup>, indicating that the potential used was insufficient to deposit a monolayer per cycle. Subsequent HgSe deposition had showed a lower Se starting coverage, 0.09 ML which increased to 0.39 ML by the 4<sup>th</sup> cycle in a period. Fig. 4.1 shows that Hg coverage started at 0.28 ML/ cycle and increased slightly to 0.32 ML by the 4<sup>th</sup> cycle. A plot of the coverage in Fig. 4.2 for the CdSe cycle shows Cd coverage decrease from 0.12 ML to 0.03 ML, with Se coverage starting from 0.031 ML to 0.024 ML. That the coverages for CdSe formation are much lower than HgSe coverages, suggests that CdSe deposition potentials are not negative enough to deposit a monolayer per cycle. Proportional coverage of HgSe to CdSe can be used to predict the stoichiometry of the CdSe/HgSe thin films, which were HgSe rich in this regard. EPMA ratios for CdSe to HgSe were 0.99 and 0.93 for the 40 and 50 period thin films respectively.

Thickness measurements of 90.71 nm (40 periods) and 151.47 nm (50 periods) were determined from the Ellipsometer. The ellipsometric measurements of the deposits showed a decrease in thickness from the inlet to the outlet, indicative of more deposition at the inlet. The refractive index measurements also change across the film, from inlet to outlet, in a similar

manner to the thickness (Fig. 4.3). The refractive index is measured as it is important to providing an accurate thickness measurement. In addition, studies relating the refractive index and energy gap have been reported, mostly for narrow band gap materials [35, 36]. The changes in refractive index across these deposits are being studied to better understand the influence of deposition conditions on the bandgap.

The deposits were a bright blue-purple color, with distinct flow patterns. Low magnification optical microscopy observation showed roughness and bubbles at the edges of the deposits (Fig. 4.4A). At higher magnification, the deposits were observed as smooth with small particles showing a slight 3D growth (Fig. 4.4B).

AFM micrographs of the gold on glass substrate and the CdSe/HgSe deposit are presented in Fig. 4.5(A & B). The substrate was rough and the deposit was made of small particles, similar to particles observed on HgSe thin films formed by EC-ALE [34]. The deposit morphology showed a possible 2D-3D growth mechanism, with CdSe preferentially growing 2D and HgSe accounting for the 3D growth. Room temperature bandgaps for CdSe and HgSe are 1.74 eV and -0.15 eV respectively. It is thus expected that the bandgap of a CdSe/HgSe thin film would lie between. The CdSe/HgSe alloy band gap structure model (Fig. 4.6) [37] indicates that the band gap changes corresponding to the concentrations (*x*) of Hg and Cd in the alloy. The stoichiometric composition of the deposit can thus be used to approximate the concentrations of Hg and Cd. CdSe/HgSe83103 had a composition of Hg<sub>0.52</sub>Cd<sub>0.48</sub>Se determined by EPMA and a band gap of 0.6 eV was suggested for X = 0.48 (Fig. 4.6). The valence band discontinuity of HgSe/CdSe formed by MBE was determined as 0.58 eV [8] and 0.73 eV for HgSe/CdSe formed by hydrogen transport CVD [7]. HgSe has an ionization potential of 1.1 eV and according to the common anion rule for forming heterostructures; the expected conduction band discontinuity is

0.64 eV [7]. A direct band gap of 0.66 eV was determined for a 40 period CdSe/HgSe thin film through a plot of  $(\alpha hv)^2$  vs. hv, shown in Fig. 4.7. The band gap of 0.66 eV determined by FTIR was in good agreement with the approximated value of 0.6 eV, and with the reported conduction band discontinuities. The XRD patterns for 40 period CdSe/HgSe deposits grown at different potentials are shown in Figs. 4.8 and 4.9. The diffraction patterns peaks of HgSe and CdSe overlap as shown in Table 4.1. The diffraction patterns observed can thus be classified as corresponding to (111), (220) and (311). The peaks match JCPDS cards 8-469 and 19-191, indicating the deposits form a zinc blende structure. Only peaks for CdSe/HgSe and the Au substrate were evident in the XRD, no elemental peaks for Hg, Cd or Se were visible. The peak pattern suggested a polycrystalline deposit, but all deposits showed a pronounced (111) peak, favored morphology.



Figure 4.1: The coverages for a 4 cycle of HgSe deposition are shown. The Hg coverage is fairly constant, and the Se coverage shows an increase with cycles deposited.



Figure 4.2: CdSe/HgSe was made alternating deposition of 4 cycles of CdSe with HgSe. Shown above is the coverage for the 4 cycles of CdSe. The decrease in coverage is obvious.



Figure 4.3: The change in the refractive index across the deposit is shown for the 40 and 50 periods CdSe/HgSe deposits.



Figure 4.4: The top micrograph (A) shows the bubble on the substrate and its effect on the deposit. Figure (B) at the bottom is the middle of the deposit at 1000X magnification, with a grey color an indication of excess Hg.



Figure 4.5: The top micrograph (A) show a substrate with a rough morphology. The micrograph at the bottom (B) shows the deposit with crystallites suggest a possible 3D growth.



Figure 4.6: Band gap structure model for the  $Hg_{1-x}Cd_xSe$  hetertostructure [37], X is the concentration distinction between Hg and Cd.



Figure 4.7: Direct energy spectra for CdSe/HgSe 40 period thin films



Figure 4.8: XRD diffraction pattern of a CdSe/HgSe (40 periods).



Figure 4.9: XRD diffraction pattern showing a 50 period CdSe/HgSe thin film.

	CdSe		
	Cubic	19-0191	
2-THETA	dA	Int.	hkl
25.3543	3.5100	100	111
42.0093	2.1490	55	220
49.6991	1.8330	25	311
	HgSe		
	Cubic	08-0469	
2-THETA	dA	Int.	hkl
25.3543	3.5100	100	111
29.3560	3.0400	16	200
41.9684	2.1510	50	220
10 6/13	1 8250	30	311

Table 4.1. CdSe and HgSe diffraction pattern data showing the peak location and the intensity expected relative to each peak.

### 4.5 CONCLUSIONS

For the first time CdSe/HgSe thin films have been formed using EC-ALE. The thin films were slightly HgSe rich, as shown by EPMA. XRD diffraction pattern showed the deposits to be cubic (zinc blende) with a preferred (111) orientation. They were conformal to the substrate, predominantly (111). The room temperature band gap of 0.66 e, was determined by FTIR and also an approximated band gap of 0.6 eV was determined from Fig. 4.6 for X = 0.48.

## 4.6 ACKNOWLEDGEMENTS

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# CHAPTER 5

HGTE deposition by electrochemical atomic layer epitaxy<sup>4</sup>

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## 5.1 ABSTRACT

HgTe thin film compound semiconductor growth by electrochemical atomic layer epitaxy (EC-ALE) is reported. EC-ALE takes advantage of underpotential deposition (upd), deposition of a surface limited amount (a monolayer or less) of an element at a potential less than that needed for bulk deposition. Thin films of compounds are formed one atomic layer at a time. HgTe thin films were formed on Au substrates using  $Hg^{+2}$  complexed with ethylenediaminetetraacetic acid (EDTA) and  $HTeO_2^+$  ions. The deposits formed were characterized by X-ray diffraction (XRD), Ellipsometry, electron probe microanalysis (EPMA), Fourier Transform Infrared spectroscopy (FTIR) and a Jenavert optical microscope. XRD analysis suggested a favored (111) texture of the zinc blende deposit. The deposits were Hg rich, with a room temperature direct bandgap of 0.15 eV.

Keywords: HgTe, EC-ALE, upd, Electrodeposition, XRD, FTIR, EPMA

#### 5.1 INTRODUCTION

HgTe is a well known mercury chalcogenide with an indirect bandgap of -0.15 eV at room temperature. Studies of HgTe/CdTe superlattices [1-5] grown by chemical beam epitaxy [6], MBE [7] and wet chemical synthesis [8], for making infrared materials [9] have been reported. HgTe has been formed by ALE [10], flash evaporation [11] and by room temperature conversion of HgO to HgTe [12, 13]. Seyam and Elfalaky[11] synthesized a p-type HgTe compound semiconductor with an energy gap of ~0.02-0.3 eV. The optical properties of HgTe, formed by MBE, have been the subject of several papers [11, 14, 15]. Zero band gap material, like HgTe, continues to be controversial: are they semimetals or semiconductors? Electrochemical atomic layer epitaxy (EC-ALE) is the electrochemical analog of atomic layer epitaxy (ALE) or atomic layer deposition (ALD), both of which are gas or vacuum phase

methods for the formation of compounds an atomic layer at a time, using surface limited reactions. Electrochemical surface limited reactions are generally called underpotential deposition (upd). Upd is used in EC-ALE to achieve monolayer by monolayer growth. Upd is the deposition of one element on a second at a potential prior to that needed to deposit the bulk element.

CdSe, CdS, and CdTe are some of the II-VI thin films that have been successfully formed electrochemically[16, 17, 18, 19]. The III-V compounds such as InAs [20] and InSb have been formed by EC-ALE as well. Initial studies of GaAs [21] and GaSb deposition have also been initiated. II-VI compound semiconductors continue to be studied in this lab [22, 23-27] and others [28-34]. IV-VI Pb compounds and their superlattices [35-41] were formed using EC-ALE.

Initial studies of the formation of HgTe on Au substrates by EC-ALE, with an automated flow deposition system, are described here. The films were characterized by means of Ellipsometry, Optical microscopy, X-ray diffraction (XRD), Electron Probe Microscope Analysis (EPMA) and Fourier Transform Infrared spectroscopy (FTIR). Optical observation of deposits indicated a roughness in their morphology, as well as flow pattern defects, especially in the middle of the deposit. The deposits showed a zinc blende structure with a major (111) peak, from the diffraction patterns. A room temperature direct bandgap of 0.15 eV was determined from absorption measurements.

#### 5.2 EXPERIMENTAL

The deposition instrument for the formation of thin films has been previously described [42]. The pump heads, valves and tubing were confined inside a  $N_2$  – purged Plexiglass box to limit the amount of oxygen present, which affects the deposit quality. The

electrochemical cell consists of a thin-layer design, to promote laminar flow. The electrodes (ITO auxiliary and Au substrate) are held apart by a silicon rubber gasket, which defines a rectangular opening where the deposition takes place. The ITO auxiliary is transparent, allowing the deposition process to be followed visually. The reference electrode, Ag/AgCl (3M NaCl) (Bioanalytical Systems, Inc., West Lafayette, IN) is positioned at the cavity outlet [43].

The HgCl<sub>2</sub> concentration was 0.2 mM, in a pH 2.0 solution complexed with 10 mM ethylenediaminetetraacetic acid (EDTA). The TeO<sub>2</sub> concentration was 0.2 mM with a pH of 9.2 buffered with sodium borate. A pH 4.0, 0.5 M Na<sub>2</sub>SO<sub>4</sub> blank solution was used. The pH of the mercury solutions pH was adjusted with H<sub>2</sub>SO<sub>4</sub>. All solutions were prepared using vacuum filtered 0.5 M NaSO<sub>4</sub>, as a supporting electrolyte. The water used to make all the solutions was supplied from a Nanopure water filtration system (Barnstead, Dubuque, IA) from the house distilled water system. The chemicals were reagent grade or better. Microscope glass slides with a 3 nm Ti adhesion layer and 600 nm Au were used as substrates. The slides were etched in a 15% HF for 60 seconds and rinsed with ultra pure water prior to insertion in the vapor deposition chamber. The substrates were annealed at 400 °C for 12 hrs before deposition [35].

The program for growth of the HgTe thin films on the gold substrates was performed as follows: The cell was filled, using a pump, from a reservoir containing an electrolyte solution of a precursor to the element of interest ( $HTeO_2^+$ ). The solution was held for 15 seconds for the deposition, and then flushed from the cell with the blank. This was followed by filling the cell with the second elemental precursor ( $Hg^{+2}$ ), and holding the solution without pumping for deposition for 15 seconds. The cycle was then completed by

flushing the second elemental precursor from the cell with the blank, and refilling with the first. This cycle ideally results in the deposition of one monolayer of the compound. The thickness of a deposit is determined by how many times the cycle is performed.

The deposits were inspected with a Jenavert microscope and their thickness measured using a single wavelength Ellipsometer (SE 400). Glancing angle X-ray diffraction patterns were acquired on a Scintag PAD V diffractometer equipped with a thin film attachment using a CuK $\alpha$  radiation, ( $\lambda = 1.5418$ Å). Absorption measurements were performed in reflection mode, using an FTIR spectrophotometer. Electron probe microanalysis studies were performed using a Joel JXA – 8600 Scanning Electron Microprobe, with a wavelength dispersive spectrometer.

XRD diffraction pattern indicated that films were zinc blende, with a preferred (111) orientation. EPMA results indicated the films had up to 20% excess mercury. A direct bandgap of 0.15 eV was measured from by reflection absorption measurements.

### 5.3 RESULTS AND DISCUSSION

The starting potentials for the deposition program were determined from the cyclic voltammograms of Hg and Te, shown in Fig. 5.1. The Hg scan was started at 0.7 V in a cathodic direction and displaced a reductive deposition peak ( $C_{II}$ ) at 0.3 V. The peak ( $C_{II}$ ) indicates a reduction of Hg<sup>2+</sup> to Hg. Reductive peak ( $C_{I}$ ) corresponds to Au oxide reduction and  $C_{III}$  to bulk deposition. Corresponding anodic peaks to reductive processes above are shown as A<sub>I</sub> to A<sub>III</sub>. The cathodic Se scan was started at 0.3 V and showed reductive peaks at -0.2 V ( $C_{I}$ ) and -0.6 V ( $C_{II}$ ). The anodic stripping peaks at 0.4 V ( $A_{II}$ ) and 0.6 V ( $A_{I}$ ) are shown in Fig. 5.2, which correspond respectively to bulk and upd stripping. Mercury and tellurium deposition potentials of 0.275 V (Fig. 5.1) and -0.20 V (Fig. 5.2) were used as starting potentials. The deposition cycle for the growth of HgTe consisted of a 2 second fill step for Te at -0.2 V, followed by 15 seconds

of deposition, with no solution flow. The cell was then rinsed with a blank solution for 3 seconds and filled for 2 seconds with the Hg precursor, after which the solution was held for 15 seconds, for deposition at 0.275 V. Finally, the Hg solution was flushed from the cell with the blank solution for 2 seconds, after Hg deposition. This cycle should form a monolayer of HgTe and was repeated to create films of different thicknesses. The deposition current time traces indicated high Hg coverage (0.7 ML) and lower Te coverage (0.3 ML), for the first 10 cycles. The potentials, however, were adjusted slightly over the first 10 cycles to better optimize the deposit. Steady state potential of 0.15 V for Hg and -0.24 V for Te for the deposits were selected and are reported here. Coverage at the steady state potentials averaged 0.61 ML for Hg and 0.30 ML for Te resulting in Hg rich deposits, confirmed by EPMA. Hg coverage decreased slightly after the first ten cycle, while Te coverage remained constant. Current time traces (Figure 5.3) shows that following Te deposition there was an oxidative spike. The oxidized species possibly might be used for the clarification concerning the low amounts of Te deposited.

Optical micrographs of HgTe deposit are shown in Fig. 5.4. Visually the deposits were purple grey in color and had a rough appearance due to flow patterns and edge effects. The deposits also appeared thicker at the edges than in the middle. At higher magnification, the deposit appeared smooth showing even coloration. The deposits appeared conformal with the morphology of the substrate.



Figure 5.1: Cyclic voltammograms of Hg [0.2 mM], pH 2.0.



Figure 5.2: Cyclic voltammograms of Te [0.2 mM], pH 9.2.

Fig. 5.5 shows a plot of deposit thickness (nm) against the number of deposit cycles, for which a linear relation is observed. The linear behavior indicates layer by layer growth as reported previously by this group [19]. The refractive index and the thickness of the deposits were measured at the inlet, middle and outlet, with using Ellipsometry. The refractive index and thickness varied slightly across the deposit, with the inlet being the thickest part of the deposit. The thickness across the deposit varies. It is somewhat thicker at the inlet, probably due to the fact that the chalcogenides deposition step is at an overpotential, in fact, and would thus depend to some extent on small variations in concentration and convection. Convection is bound to be larger at the entrance, before laminar flow is achieved. The stoichiometric ratio of the deposit determined by EPMA measurements, showed deposits to be generally mercury rich, by about 20%. The stoichiometry and current time traces indicate that less than optimal conditions were used to form these deposits. Optimization of deposition conditions should improve stoichiometry, as well as promote ML/ cycle deposition. A ML/cycle is defined as one atom per Au(111) surface with an atom equal to 1.0 ML. Present deposits have shown average coverages of 0.6 ML per cycle for Hg and 0.3 ML for Te. Optimized deposition conditions should result in equal deposition of Hg and Te, and thus achieve layer by layer growth. The diffraction pattern obtained for EC-ALE deposited HgTe is shown in Fig. 5.6. The particle size was calculated using the Scherrer equation to be 20.27 nm. Peaks corresponding to (111), (200), (220), (311), (400) and (331) planes of HgTe are shown on the diffraction pattern. The peaks match the JCPDS card 8-469, indicating a zinc blende structure. The peak pattern suggested a polycrystalline deposit and all deposits showed a pronounced (111) peak, a favored morphology. There was no indication of elemental diffraction peaks for Hg or Te, only peaks for HgTe and the Au were present.

The absorption measurements were performed at room temperature, on a deposit with a ratio of 1.25, Hg/Te. A plot of  $\alpha$  vs. *hv* is presented in Fig. 5.7, from which a bandgap value of 0.15 eV was determined by extrapolating a straight line to the x-axis.



Figure 5.3: Current time traces for HgTe deposition, showing the Hg and Te deposition changes over the first 11 cycles. Te was deposited first in these studies.



Figure 5.4: Optical micrographs, the top micrograph (A) shows the bubble effect at the edge of the gasket. Micrograph (B) at the bottom is the middle of the deposit showing uniform growth.



Figure 5.5: Thickness of the deposited was measured by the Ellipsometer for deposits with a different number of cycles. A next to linear relation indicates a probable layer by layer growth.



Figure 5.6: An XRD diffraction pattern of HgTe71603 showing the HgTe peaks with no indication of elemental peaks of Hg or Te. Au substrate peaks were also obvious. The pronounced HgTe (111) peaks indicates a that the deposit is polycrystalline.



Figure 5.7: A plot of  $\alpha$  vs. *h*v for the absorption measurements of HgTe done at room temperature

# 5.5 CONCLUSIONS

The initial studies in the formation of HgTe by EC-ALE have been reported. A direct band gap of 0 eV was deduced from room temperature optical absorption measurements, which is expected for a semimetal. The XRD diffraction pattern showed a preferred (111) orientation. The use of Au single crystal substrates will assist in the determination of the quality of the deposits, once deposition conditions are optimized.

# 5.6 ACKNOWLEDGEMENTS

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# CHAPTER 6

# MODELING QUANTUM CONFINEMENT IN PBSE THIN FILMS FORMED USING

EC-ALE<sup>5</sup>

<sup>&</sup>lt;sup>5</sup> M. K. Mathe, S. M. Cox, R. Vaidyanathan, U. Happek and J.L. Stickney to be submitted to *Journal of Applied Physics* 

# 6.1 ABSTRACT

PbSe thin films formed by EC-ALE on Au substrates were studied for quantum confinement effects using optical absorption methods. PbSe deposits showed a bandgap decrease with an increase in the number of cycles deposited, suggestive of quantum confinement due to thickness. Results were compared to a parabolic and a hyperbolic band models. X-ray diffraction patterns indicated that the PbSe thin films formed were of a rock salt structure, polycrystalline, and had a prominent (200) peak. The EPMA data showed the deposits were stoichiometric, with a little Se excess.

Keywords: PbSe, EC-ALE, quantum confinement, effective mass approximation, hyperbolic band model, bandgap, XRD, EPMA

### 6.2 INTRODUCTION

Lead selenide, a narrow bandgap IV-VI compound semiconductor has a 0.26 eV room temperature bandgap. PbSe has been formed by molecular beam epitaxy [1], chemical bath deposition [2], successive ionic layer adsorption [3], and electrodeposition [4-11]. Optical and photoconductivity studies of PbSe have been reported [12-14]. Electrochemical quartz crystal microbalance (EQCM) [9] was used to study the mechanism for PbSe Electrodeposition. PbSe. A unique role for cadmium in the electrodeposition of PbSe has also been studied [6, 7, 10, 11, 15], and indicated Cd influences the PbSe crystal structure.

Recently, the formation of PbSe by electrochemical atomic layer epitaxy (EC-ALE) was reported [16]. EC-ALE is the electrochemical analog of atomic layer epitaxy (ALE), and makes use of underpotential deposition (upd) to electrodeposit single atomic monolayers of the elements, making up a compound semiconductor. Upd is a well-documented phenomenon in which one-element deposits onto another element at a potential prior to (under) that necessary to
deposit the element onto itself. The resulting deposit is limited to an atomic layer. This is due to the surface limited nature of upd, which results in a structure that is independent of mass-transport. EC-ALE has been used in the formation of II-VI [17-23], III-V's [24-26] and IV-VI [16, 27]compounds.

In this work, absorption measurements were performed on PbSe thin films deposits formed using EC-ALE, to study quantum confinement effects. Deposits made were also characterized for stoichiometry (EPMA), crystal structure (XRD) and morphology (AFM). Absorption studies indicated that the bandgap of the films decreased with an increase in the thickness of the deposits, an apparent indication of confinement.

#### 6.3 EXPERIMENTAL

PbSe thin films modeled for quantum confinement effect were formed using an automated electrochemical thin-layer flow deposition system. The deposition system has been previously described [24, 26, 28, 29]. The system contained within a nitrogen purged Plexiglas box consists of: a potentiostat, computer controlled pumps and valves, as well as solution reservoirs. Nitrogen purging reduces the oxygen levels in solutions resulting in better quality deposits. A three electrode cell used consisted of a Au working electrode, Au coated indium tin oxide (ITO) auxiliary electrode and Ag | AgCl (3M NaCl) reference electrode (Bioanalytical systems, Inc., West Lafayette, IN). The deposition cell was designed to promote laminar flow.

Solutions were prepared using reagent grade or better chemicals, with water from a Nanopure water filtration system (Barnstead, Dubuque, IA) fed by the in house, deionized water supply. Solutions used were made using a 0.1 M NaClO<sub>4</sub> (Fischer Scientific, Pittsburgh, PA) supporting electrolyte. These included: 0.2 mM Pb (ClO<sub>4</sub>)<sub>2</sub> (Alfa Aesar, Ward Hill, MA), pH 5.5, buffered with 50.0 mM CH<sub>3</sub>COONa·3H<sub>2</sub>O (J.T.Baker); 0.2 mM

SeO<sub>2</sub> (Alfa Aesar, Ward Hill, MA), pH 5.5, also buffered with 50.0 mM  $CH_3COONa \cdot 3H_2O$ . A pH 5.5 rinse solution (0.1 M NaClO<sub>4</sub>) without a buffer was used as well. The pH values of all solutions were adjusted with  $CH_3COOH$  (Fischer Scientific, Pittsburgh, PA).

Microscope glass slides with a 3 nm Ti adhesion layer and 600 nm Au were used as substrates. The slides were etched in a 15% HF for 60 seconds and rinsed with ultra pure water prior to insertion in the vapor deposition chamber. The substrates were annealed at 400 °C for 12 hrs before deposition [16].

The deposits were inspected with a Jenavert microscope. Ellipsometric measurements were performed using a single wavelength Sentech SE 400 (Micro Photonics Inc., Allentown, PA). Glancing angle X-ray diffraction patterns were acquired on a Scintag PAD V diffractometer equipped with a thin – film attachment using CuK $\alpha$  radiation, ( $\lambda = 1.5418$ Å). Electron probe microanalysis (EPMA) was run on a Joel 8600 scanning electron microprobe, with a wavelength dispersive spectrometer. AFM studies were performed using a Nanoscope 2000 (Digital Instruments, Santa Barbara, CA) in the tapping mode. Absorption measurements were performed using an FTIR spectrometer.

#### 6.4 RESULTS AND DISCUSSION

Cyclic voltammograms of Pb and Se solutions are shown in Fig. 6.1, and were used to determine suitable starting potentials for the deposition of PbSe. A starting upd potential of -0.2 V was chosen for both Pb and Se. The deposition program started with a 2 second fill step for Pb at -0.2 V, which was then deposited for 15 seconds with no solution flowing. Following deposition, the cell was rinsed for 3 seconds with a blank and filled with Se at -0.2 V for 2 seconds. Se was deposited for 15 seconds with no solution. The Se solution was rinsed out of the

cell with blank for 3 seconds. The cycle was repeated to form deposits of 5 to 100 cycles, with each cycle forming a monolayer of PbSe. Slightly higher Se ML/cycle coverages were observed compared to Pb ML/cycle coverage.

Fig. 6.2 shows amounts of Pb and Se deposited per cycle in the formation of PbSe. The deposition current time traces were integrated for both Pb and Se, to establish the amounts deposited. The figure indicates that lower amounts of Pb were deposited over the first 10 cycles, following which the Pb amounts deposited are almost 90% of the Se deposited per cycle. The potentials were then stepped over the first 10 cycles to compensate for these lower initial coverages, such that ML/cycle deposition was realized. The need to ramp potentials over the first few cycles has been studied by this group [24-26, 29, 30], with the understanding that the upd potential determined from voltammetry , were only applicable to a first few layers. The progression in deposition requires the potentials to be adjusted to maintain ML/cycle deposition. The ML/cycle coverage for both Pb and Se are shown in Fig. 6.2. The coverages indicated that the deposited amounts were approximately equal, as the cycles progressed.

The stoichiometric ratios of Se/Pb shown in Table 6.1 indicate that the deposits were Se rich. The data presented in Table 6.1 shows agreement with coverage results (Fig. 6.2). The thickness of the deposits was measured by Ellipsometry and showed an increase relative to the number of cycles deposited, indicated in Table 6.1. Subsequently, the amount deposited past the first 10 cycles was close to the expected ML/cycle coverage. The resulting deposits were dark blue in color, as observed visually and through the microscope.

X-ray diffraction patterns for a 100 and an 85 cycle deposit are shown in Fig. 6.3. Peaks corresponding to (111), (200), (220), (311), (400) and (420) planes matching rock salt [JCPDS

06 - 0354], PbSe are shown. A dominant peak (200) was observed in both patterns with a ratio of (200)/(111) peaks being 3.10 and 3.42. The ratio of the peaks (200)/(100) from [JCPDS 06-0354] card is 3.33 for a polycrystalline deposit. The ratios determined from the diffraction patterns indicate that the deposits formed were polycrystalline. The particle sizes for a 100 cycle deposit and an 85 cycle deposit were calculated using the Scherrer equation, and determined to be 18.78 nm and 15.80 nm respectively. Figs 6.4 and 6.5 show AFM micrographs of the Au substrates and the PbSe deposits having different thickness. The micrograph (Fig 6. 4A) compared to Fig 6.5A, clearly indicates a difference in the Au substrate quality used to deposit PbSe thin films. The substrate shown in Fig 6.4A shows an even morphology, related to deposit morphology (Fig 6.4B). The substrate and deposit in Figs 6.5A and 6.5B show a rough morphology. Ideally, flat or smooth substrates are favored and would in general result in layer by layer growth of the deposits. PbSe thin films of various thicknesses (5 - 85 cycles) were studied for quantum confinement effects by FTIR spectroscopy. Plots of transmittance are presented in Fig 6.6A (85 cycles) and Fig 6.6B (30 cycles). Studies were performed for a series of deposits, as presented in Table 6.1. Plots of  $\alpha^2$  vs. hv are usually used to determine the direct bandgaps of a semiconductors formed by EC-ALE. For the plots reported here,  $d\alpha/d(h\nu)$  vs. hv was used based on detailed studies on the anomalies related to determining the bandgap for Pb compounds [31]. The bandgaps were determined from the first considerable peaks on the plots (Figs. 6.6A & 6.6B). The bandgaps presented in Table 6.1 were also determined in the same manner. Fig. 6.8 shows plots of the E<sub>g</sub> data presented in Table 6.1, as a function of the number of PbSe cycles deposited (dots), fitted against the hyperbolic band model (solid & dotted lines). The band model was used to show a correlation between the film thickness and the effective mass



Figure 6.1: Top is the cyclic voltammograms of Pb [0.2 mM], pH5.5 and the bottom cyclic voltammograms is HSeO<sub>3</sub><sup>-</sup> [0.2 mM], pH 5.5. Solutions were made using 0.1 M NaClO<sub>4</sub> as an electrolyte.



Figure 6.2: The ML/cycle coverage for a PbSe 30 cycle deposit shows amounts deposited for Pb and Se per cycle.

Sample	# of cycles	Theoretical Th (nm)	Experimental Th (nm)	EPMA Se/Pb	E <sub>g</sub> (eV)
	, i i i i i i i i i i i i i i i i i i i				1.214
					1.156
PbSe6/11/034	10	3.3	3.86	1.18	1.119
					0.752
					0.560
PbSe6/11/033	15	5.3	4.28	1.33	0.548
					0.811
PbSe6/11/032	20	7.07	4.31	Х	0.715
					0.532
					0.532
PbSe6/11/03	30	10.61	14.07	1.23	0.527
					0.329
PbSe5/12/03	85	30.05	111.52	1.06	0.312

Table 6.1: Thickness (nm), EPMA and bandgap data for PbSe deposits made with different number of cycles.



Figure 6.3A: XRD diffraction pattern of a 100 cycle PbSe deposit showing the PbSe and Au peaks. The elemental peaks for Pb and Se were not observed. The particle size was calculated using the (200) peak.



Figure 6.3B: XRD diffraction pattern of an 85 cycle PbSe deposit showing the PbSe and Au peaks. The elemental peaks for Pb and Se were not observed. The particle size was calculated using the (200) peak.

approximations. Equations (1) and (2) were used to calculate the theoretical  $E_g$  by using the values on Table 6.2 [32, 33]. The deposit thicknesses used in Fig 6.8, taken from Table 6.1, were calculated by means of the hypothesis that the growth of PbSe was in a (111) direction with a 6.124Å lattice constant [31]. The experimental thicknesses were measured with an Ellipsometer and are strongly matched to the theoretical thicknesses, with the exception of the 85 cycle deposit. The ellipsometric thickness measurement of the 85 cycle deposit (111.52 nm) was not useful, as it was far from the theoretical value (30.02 nm), possibly due to roughening in the deposit.

On both Figs. 6.7A and 6.7B, the bandgap of the PbSe deposits indicates a decrease with an increase in the number of cycles. The literature value for the PbSe bandgap is 0.26 eV, and from Table 6.1, it is obvious that by increasing the number of cycles, a thickness can be reached where the measured bandgap should equal the bulk  $E_g$  literature value, Figs. 6.7A and 6.7B. The hyperbolic and parabolic band models show agreement between the theoretical values used and experimental values determined for quantum confinement effects on PbSe thin films formed by EC-ALE.

The parabolic band model using equation [33](1) and values on Table 6.2 was used to show the trend in absorption for the PbSe deposits with different thicknesses. Fig. 6.7 depicts a relationship between the bandgap and the theoretical thickness of the deposits. The dots shown of Fig. 6.7 are the experimental values measured for the PbSe deposits, their bandgap values are in agreement with the parabolic band model.

The hyperbolic band model was also used and compared to the parabolic model. The bandgap values for the hyperbolic model were calculated using equation (2) and values on Table 6.2. The plots of  $d\alpha/d$  (*hv*) are shown in Fig. 6.7, and a good agreement between the parabolic, hyperbolic and experimental values showing the quantum confinement effect in the PbSe deposits with differing thickness.

$$E_{\rm g} = \sqrt{E_{\rm g,bulk}^2 + 4 \frac{\hbar^2 \pi^2}{2m^* L^2} E_{\rm g,bulk}}$$
 (2)



07131332.001 Pbse 6/11/03-2, AU SUB



Figure 6.4: The top micrograph is for rough Au substrate. Bottom micrograph is for a 20 cycle PbSe deposit.



07131803.001 PbSe 5/17/03, AU SUB



Figure 6.5: Micrograph on top shows a Au substrate with large terraces. The bottom micrograph is the PbSe deposit showing small crystallites.



Figure 6.6: The absorption spectra of an 85 cycle PbSe deposit is shown at the top. At the bottom is the spectrum for a 30 cycle deposit. The bandgap values from these graphs are presented in Table 6.1.

Ref	$m^*_{e}/m_{e}$	$m^*_{\rm h}/m_{\rm e}$	$\mu/m_{\rm e}$	$m^*/m_e$
[32]8}	0.050	0.045	0.022	0.048
[33]7}	0.084	0.070	0.038	0.077

Table 6.2: Literature values used for the computations of the bandgap values for the Hyperbolic and Parabolic band models.

The parameters used in equations (1) and (2) have their usual meanings. In Fig 6.7, the solid line on both graphs corresponds to reference 32 on table above. The dotted lines on both graphs on Fig.6.7 correspond to reference 33, above. For the hyperbolic model, the coverage factor was used was calculated from coulometric data to better approximate the thickness of the films.



Figure 6.7: The plots of  $d\alpha/d$  (*hv*) above depict the bandgap data presented in Table 6.1. Table 6.2 values were used with equations (1) and (2), respectively for the parabolic (top graph - A) and hyperbolic band models (bottom graph - B).

## 6.5 CONCLUSIONS

PbSe thin films formed by EC-ALE on Au substrates showed good stoichiometry, a rock salt structure with a pronounced (200) diffraction peak. The deposits exhibited quantum confinement effects with bandgap decrease when the number of layers deposited increases. The theoretical thicknesses used in these studies were confirmed by the ellipsometric measurements except for one point. Changing the thickness of the deposits by deposition of fewer layers has shown that the bandgap can be blue shifted.

#### 6.6 ACKNOWLEDGEMENTS

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# CHAPTER 7

# PBTE/PBSE SUPERLATTICE FORMATION BY ELECTROCHEMICAL ATOMIC LAYER

EPITAXY<sup>6</sup>

<sup>&</sup>lt;sup>6</sup> M. K. Mathe, S. M. Cox, R. Vaidyanathan, U. Happek and J. L. Stickney to be submitted to *Journal of Crystal Growth* 

## 7.1 ABSTRACT

PbTe/PbSe superlattices formed by electrochemical atomic layer epitaxy (EC-ALE) were investigated for absorption at room temperature by FTIR. The absorption measurements showed a decrease in bandgap with an increase in the number of layers in a period, suggestive of quantum confinement. Steps were observed on the absorption spectra indicative of energy transitions. The superlattices formed using a series of alternated PbTe and PbSe cycles in a period, were Se rich as measured by EPMA.

Keywords: PbTe/PbSe, EC-ALE, bandgap, FTIR, EPMA

#### 7.2 INTRODUCTION

The formation of superlattices was pioneered by Esaki [1], and resulted in the explosive growth in the study of nanostructures. New materials can now be produced by combining different bandgap compound semiconductors. The bandgap of the new material can be engineered by changing the thickness of the layers in the superlattice.

Lattice match is important in designing superlattices. The lattice match is a comparative measure of the crystal structure lattice of constituent compounds, which for PbTe (6.460Å) and PbSe (6.124 Å), results in a mismatch of 5.2% ( $\Delta a/a$ ) [2]. Nanostructures of various combinations of compound semiconductors, have been formed by physical [3-5] and chemical methods [6-10].

A superlattice is formed by the deposition of alternating layers of two compound semiconductors with different band gaps that are lattice matched. The presence of satellite peaks in the XRD diffraction pattern is strong evidence that a superlattices has been formed [8].

IV-VI nanostructures have been reported as potentially useful as thermoelectric materials [11-13], waveguides [14], infrared sensors [3] as well as other applications. The PbTe/PbSe

structure is appealing to study due to the large Bohr radii of PbTe (50 nm) and PbSe (46 nm), as it suggests that large period superlattices should still display quantum confinement effects.

Studies of PbSe/PbTe superlattices formation by codepostion [15-18], and also by electrochemical atomic layer epitaxy (EC-ALE) recently [19] were reported.

EC-ALE is a promising electrochemical methods presently used by this lab and others. EC-ALE is the electrochemical analog of atomic layer epitaxy (ALE). ALE is based on the use of surface limited reactions. Electrochemical surface limited reactions are referred to as (UPD), and EC-ALE makes use of underpotential deposition (upd) to electrodeposit single atomic monolayers of the elements making up a compound semiconductor. Upd is a well-documented phenomenon in which one-element deposits onto another element at a potential prior to (under) that necessary to deposit the element onto itself. The resulting deposit is limited to an atomic layer, as upd can be thought of as the formation of a surface compound or alloy, and when the surface is used up, deposition stops.

EC-ALE has been used to formation of II-VI [20-25], III-V's [26-28] and IV-VI [29-31]compounds. In this article, the growth of PbTe/PbSe superlattices of different thicknesses by EC-ALE is reported. Absorption measurements of PbTe/PbSe superlattices were investigated to determine the layer thickness on the deposit bandgap, and how the bandgap decreased as the superlattice period increased. The superlattices were characterized for stoichiometry by EPMA and the crystal structure determined by XRD.

#### 7.3 EXPERIMENTAL

An automated electrochemical thin-layer flow deposition system was used to form PbTe/PbSe nanostructures, and has been previously described [26-28, 32-34]. The system consists of: a potentiostat, computer controlled pumps and valves, as well as solution reservoirs, contained

within a nitrogen purged Plexiglas box. Nitrogen purging reduces the oxygen levels in solutions resulting in better quality deposits. A three electrode cell used consisted of a Au working electrode, Au coated indium tin oxide (ITO) auxiliary electrode and Ag | AgCl (3M NaCl) reference electrode (Bioanalytical systems, Inc., West Lafayette, IN). The deposition cell used had laminar flow, desirable for homogeneous deposition.

Solutions were prepared using reagent grade or better chemicals, with water from a Nanopure water filtration system (Barnstead, Dubuque, IA), fed by the in house deionized water system. Solutions used were made with a 0.1 M NaClO<sub>4</sub> (Fischer Scientific, Pittsburgh, PA) supporting electrolyte. Solutions included: 0.2 mM Pb (ClO<sub>4</sub>)<sub>2</sub> (Alfa Aesar, Ward Hill, MA), pH 5.5, buffered with 50.0 mM CH<sub>3</sub>COONa·3H<sub>2</sub>O (J.T.Baker); 0.2 mM SeO<sub>2</sub> (Alfa Aesar, Ward Hill, MA), pH 5.5, also buffered with 50.0 mM CH<sub>3</sub>COONa·3H<sub>2</sub>O; and a 0.2 mM TeO<sub>2</sub> (Alfa Aesar, Ward Hill, MA), pH 9.2, buffered with 50.0 mM Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>. A pH 5.5 rinse solution (0.1 M NaClO<sub>4</sub>) was used as well. The pH values of all solutions were adjusted with CH<sub>3</sub>COOH (Fischer Scientific, Pittsburgh, PA) with the exception of the Te solution, pH 9.2.

Glass microscope slides, with a 3 nm Ti adhesion layer and 600 nm Au were used as substrates. The slides were etched in a 15% HF for 60 seconds and rinsed with ultra pure water prior to insertion in the vapor deposition chamber. The substrates were annealed at 400 °C for 12 hrs before deposition [30].

The deposits were inspected with a Jenavert optical metallographic microscope. Ellipsometric measurements were performed using a single wavelength Sentech SE 400 (Micro Photonics Inc., Allentown, PA). Glancing angle X-ray diffraction patterns were acquired on a Scintag PAD V diffractometer equipped with a thin film attachment, using CuK $\alpha$  radiation, ( $\lambda$  = 1.5418Å). Electron probe microanalysis (EPMA) was run on a Joel 8600 scanning electron microprobe, with a wavelength dispersive spectrometer. A Nanoscope 2000 AFM (Digital Instruments, Santa Barbara, CA), was used in the tapping mode to study the morphology of the PbTe/PbSe nanostructures formed by EC-ALE. The FTIR spectrometer used for absorption studies of the nanostructures was a Bruker TSS-66v, Bruker Optics, Inc.

#### 7.4 RESULTS AND DISCUSSION

PbTe and PbSe buffer layers were used to form nanostructures of PbTe/PbSe using EC-ALE. The cyclic voltammograms for the Pb, Te and Se solutions used in these studies were reported elsewhere [19, 29, 30]. The starting deposition potentials for the formation of PbTe and PbSe have also been reported [29, 30]. In these studies, the starting potentials used to form PbTe were -0.26 V for Pb and -0.38 V for Te. The potentials were used throughout the deposition without ramping. The PbSe potentials used were -0.2 V for both Pb and Se. Nanostructures consisting of 2, 3, 5 and 6 layers each for PbTe and PbSe were alternated to form 40 and 80 period superlattices. A 10 cycle PbTe buffer layer was used for the 2, 5 and 6 layered superlattices, and a 30 cycle buffer layer was used for the superlattice where 3 layers were used

Te was deposited first in the formation of PbTe, whereas, Pb was deposited first in the formation of PbSe. The cycle used in the formation of PbTe was performed as follows: Te was rinsed into the cell at -0.38 V for 2 seconds. The solution flow was then stopped for 15 seconds while Te was deposited. The cell was then rinsed with the blank for 2 seconds, and then Pb was rinsed in at -0.26 V for 3 seconds followed by 15 seconds with no solution flow. The cell was then rinsed again with the blank, completing one cycle and the deposition of a ML of PbTe. The cycle can then be repeated to grow correspondingly in connection to the thicker layers.

PbSe cycles were formed by rinsing in Pb at -0.2 V for 2 seconds, and depositing for 15 seconds with no solution flowing. The cell was then rinsed with blank, followed by a 2 seconds fill with the Se precursor at -0.2 V. Again the solution was held for 15 seconds for deposition.

The programs described above were repeated for each compound for the required number of layers, forming a period. For instance, the 2 cycle superlattice was formed by performing 2 cycles of PbTe alternated with 2 cycles of PbSe. Table 7.1 lists the compositions of different superlattices attempted. EPMA data in Table 7.1 indicates that the superlattices formed were, to some extent, Se rich.

Ellipsometry data shows a related increase in thickness with the number of layers deposited. Fig. 7.1 shows a plot of thickness vs. periodicity, and a close to linear correlation was obvious for superlattices of periodicities of 3 through 6. The anomalous point in thickness on the graph was SL81803 (91.58 nm), an 80 period superlattice, all other superlattices formed were 40 periods thick. The corresponding increments between thickness and periodicity suggested layer by layer growth in the formation of the superlattices.

The modulation wavelength ( $\Lambda$ ) of the superlattices, also known as the period (H), can be calculated from the diffraction pattern of the resulting superlattice. The presence of satellite peaks in the diffraction patterns serves as a measure of the quality of the superlattice formed. The satellite peaks for a superlattice with well resolved interfaces between compounds modulated will be sharp and well resolved. However, intermixing might occur between the modulated compounds, resulting in a quasiperiodic superlattice [35].

The diffraction patterns of superlattices reported in this study did not show distinctly resolved satellite peaks. The diffraction patterns shown in Figs. 7.2 and 7.3, for 3:3 and 5:5 superlattices, respectively, had faint satellite peaks on the (200) Bragg diffraction peak. The

modulation wavelengths ( $\Lambda$ ) for the superlattices shown in Figs. 7.2 and 7.3 were calculated using equation (1) and are listed in Table 7.1.

where  $\lambda = 0.15418$  nm and -n and + n are the same order adjacent satellite peaks on the main Bragg peak [8].

The periodicity for the 5:5 superlattice was calculated using n = 2, and for the 3:3 superlattice, n = 1 was used. The choice of the n value was based on the equidistance from the (200) Bragg diffraction peak.

Table 7.2 shows the JCPDS cards for PbSe and PbTe, which can be used to explain the peak broadening, observed in the diffraction patterns (Figs. 7.2 and 7.3). The diffraction patterns of these superlattices and the absorption spectra shown in Fig. 7.4, suggests that, the superlattices can be termed, quasiperiodic Fibonacci superlattices. The Fibonacci superlattices are characterized by lack of distinct satellite peaks, and the steps shown in Fig. 7.4, represent the energy transitions in the superlattice. The steps were, in addition, attributed to the density of states function [35]. The step patterns in Fig. 7.4 shows the blue shift related to the decreasing periodicity, due to quantum confinement effects.

Table 7.1: Data representing the difference in thickness, bandgap and stoichiometry for superlattices formed with different number of layers in a period.

Sample	Layers	EPMA	Thicknes	Eg	Period
	PbTe:		S	(eV)	$\Lambda$ (nm)
	PbSe		(nm)		
SL71703	6:6	PbTe <sub>0.43</sub> Se <sub>0.57</sub>	151.02	0.22	Х
SL72103	5:5	PbTe <sub>0.46</sub> Se <sub>0.53</sub>	114.59	0.32	4.96
SL71203 <sup>+</sup>	3:3	PbTe <sub>0.41</sub> Se <sub>0.59</sub>	82.54	0.41	2.58
SL81803	2:2	PbTe <sub>0.47</sub> Se <sub>0.53</sub>	91.58 <sup>*</sup>	0.47	X

<sup>+</sup> grown on 30 cycle PbSe buffer layer.

\* 80 periods of PbTe/PbSe superlattice.



Figure 7.1: Thickness vs. periodicity plot for PbTe/PbSe superlattice grown by EC-ALE

FN: SL72103.RD DATE: 07/29/03	ID: 10: TIME: 10: 2	5:5 40 PERIOD 1 PT:0.90	S PBTE/PBSE 000 STEP:	0.03000	SCINTAG/USA WL: 1.54060
CPS 4.436	2.976 I		1.823	1.541	1.343%
900.9-					- 90
800.8-					- во
600.6-					- 60
400.4-					- 40
300.3-					- 30
200.2-					- 20
100.1-	w lun	NVW	MA		- 10
0.0	30	40	50	60	

Figure 7.2: Diffraction pattern of a PbTe/PbSe grown on a 10 cycle PbTe buffer layer. The alternated cycles were 5 cycles PbSe followed by 5 cycles PbTe, repeated to form a 40 period deposit. The periodicity of the superlattices was calculated as 4.96 nm using equation (1).

FN: SL71703.RD DATE: 07/29/03	ID: 1 TIME: 11: 4	0:6:6 40 PERIO 1 PT:0.90	DS PBTE/PBSE 000 STEP:	0.03000	SCINTAG/USA WL: 1.54060
CPS 4.436 767.0	2.976	2.252	1.823	1.541	1.343 %
690.3-					- 90
613.6-					- 80
536.9-	1				- 70
460.2-					- 60
383.5-					
306.8-					- 40
230.1-					- 30
153.4-	N	INV I			- 20
76.7- N	Co Manumeron	N. VI	waynowyan	manutara	- 10
0.0	30	40	50	60 60	70

Figure 7.3: Diffraction pattern of a PbTe/PbSe grown on a 10 cycle PbTe buffer layer. The alternated cycles were 6 cycles PbSe followed by 6 cycles PbTe, repeated to form a 40 period deposit.

PbSe	06-0354		PbTe	38-1435
2-THETA	Int.	hkl	2-THETA	Int.
25.1648	30	111	23.8240	8
29.1404	100	200	27.5719	100
41.6843	70	220	39.4103	75
49.3257	18	311	46.5829	4
51.6581	20	222	48.7911	23
60.4148	14	400	56.9718	17
66.4148	6	331	62.6300	2
68.4813	25	420	64.4421	27
76.0836	16	422	71.4928	18
81.5887	4	511	76.5654	9

Table 7.2: JCPDS card files for PbSe and PbTe showing the peak location and intensities expected on the diffraction patterns.



Figure 7.4: The absorption spectra for PbTe/PbSe of different periodicities, the bandgap of each are presented in Table 7.1.

## 7.5 CONCLUSIONS

The formation of PbTe/PbSe superlattices of different periodicities has been reported. The absence of well resolved satellite peaks was shown to result from possible intermixing between PbTe and PbSe and the 5% lattice mismatch. The improvement of distinct interfaces can be achieved by using optimized deposition program for PbTe and PbSe.

## 7.6 ACKNOWLEDGEMENTS

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# CHAPTER 8

# CONCLUSIONS AND FUTURE STUDIES

The formation of II-VI compounds CdSe, HgSe and HgTe by EC-ALE was demonstrated. The deposits formed of CdSe and HgSe were generally stoichiometric as shown by EPMA measurements, for optimized conditions. HgTe deposits were Hg rich, as the conditions used were not yet most optimized. Optimization of HgTe deposition conditions is ongoing. There is a strong driving force to form MCT by EC-ALE and the formation of HgTe is an important step. The diffraction patterns of deposits had preferred (111) orientations, which was in good agreement with the predominantly (111) Au substrates used.

The first attempt in the formation of CdSe/HgSe was also reported with encouraging results. Additional studies of this system are crucial for the understanding of the optical properties, as they will establish its industrial use.

Deposition of PbSe thin films and PbTe/PbSe superlattices by EC-ALE was reported. PbSe was studied for quantum confinement effects by absorption measurements, and showed a decrease in bandgap with an increase in the number of cycles deposited. Attempts at the formation of PbTe/PbSe superlattices suggest the need for further studies, as the satellite peaks anticipated for the superlattices were not obvious. PbTe/PbSe superlattices formed were generally Se rich as indicated by EPMA data.

The reproducibility of forming the deposits is encouraging, and characterization using different techniques showed improvement in the quality of the deposits, when most favorable conditions are used.

For future studies, the formation Hg chalcogenides compounds create an exciting possibility of forming  $Hg_{1-x}Cd_xTe$  heterostructures (thin films) by EC-ALE. The formation of CdSe using different electrolytes as such as sodium perchlorate, will create more possibilities for forming CdSe, and should be pursued. In these studies the importance of good substrates was
demonstrated by XRD diffraction patterns that had pronounced (111) diffraction peaks. The study on the deposition of substrates and the exploration of using semiconductor substrate should be pursued. The need for additional characterization techniques that may well be used to investigate electrical and photoelectrochemical properties is obvious.