Electrochemical atomic layer epitaxy (EC-ALE) has been developed in this research group to electrochemically prepare thin films of compound semiconductors. It is an electrochemical analog of atomic layer epitaxy (ALE), where a compound is grown in layer-by-layer fashion. A surface limited reaction, underpotential deposition (UPD), is used to deposit constituent elements one monolayer at a time. The EC-ALE promotes two-dimensional growth, resulting in better control of composition and structure in deposited film than conventional electrochemical co-deposition.

The composition of films grown using EC-ALE is initially approximated from the charges passed during depositions. Faraday’s law is used to calculate the amounts of deposited elements. In general, the coulometric results indicate the films are off stoichiometric. However, electron microprobe analysis (EPMA) suggests otherwise, that the films are quite stoichiometric. The differences may correspond to side reactions, such as hydrogen evolution, oxygen reduction, and contaminants, which result in extra charges and errors in the composition calculations.

An electrochemical quartz crystal microbalance (EQCM) is capable of measuring small mass changes on its surface. A flow cell EQCM was constructed to study the formation of
various metal chalcogenides using EC-ALE. The detailed description of the flow cell EQCM is described. The design of the flow cell currently used in this laboratory was modified to accommodate the quartz crystal oscillator. Two pumping methods (He pressure and peristaltic pump) were used to flow solutions with acceptable noise level in $\Delta f$ measurements. Higher solution flow rates were obtained by using the peristaltic pump. When solution flow was stopped, shifts in $\Delta f$ values were observed, associated with changes in pressure.

The flow cell EQCM was used to grow CdSe and PbTe. Cyclic voltammetry was used to determine UPD and bulk potentials for each element. A series of depositions was carried out with various deposition programs using the UPD potentials. Both current and $\Delta f$ were measured as a function of deposition time and used to calculate coverages of deposited elements. With these results, it was determined that extra charges corresponded to the reduction of oxygen dissolved in deposition solutions. The optimized deposition programs for CdSe and PbTe were also suggested.

INDEX WORDS: Electrochemistry, Electrodeposition, Thin film, Compound semiconductor, Electrochemical atomic layer epitaxy, EC-ALE, Atomic layer epitaxy, ALE, Underpotential deposition, UPD, Quartz crystal microbalance, QCM, Electrochemical quartz crystal microbalance, EQCM, Flow cell, Metal chalcogenide, CdSe, PbSe, PbTe, The University of Georgia
ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE (EQCM) STUDIES OF
COMPOUND SEMICONDUCTOR FORMATION BY EC-ALE

by

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A Dissertation Submitted to the Graduate Faculty of The University of Georgia in Partial
Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

ATHENS, GEORGIA

2004
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August 2004
DEDICATION

To My Family: Boonmee, Phuchong, Ekaruth, and Manruth
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my research advisor, Professor John L. Stickney, for his advice and encouragement during my Ph.D. study. Also, I would like to thank Professors James L. Anderson, I. Jonathan Amster, and Richard A. Dluhy for serving on my advisory committee.

I also would like to thank Thai government for giving me the financial support through a Royal Thai Government Scholarship. Joeseph Brezner, I am grateful for your help on designing and writing LabView programs. The special notes of thanks are offered to the past and present members of Professor Stickney’s laboratory for their friendship and memorable times.

At last, my parents (Boonmee and Phuchong Srisook) as well as my elder brothers (Ekaruth and Manruth Srisook), I thank them the most for their support in all these years.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>FLOW CELL ELECTROCHEMICAL QUARTZ CRYSTAL</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>FLOW CELL ELECTROCHEMICAL QUARTZ CRYSTAL</td>
<td>53</td>
</tr>
<tr>
<td>4</td>
<td>FLOW CELL ELECTROCHEMICAL QUARTZ CRYSTAL</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>CONCLUSIONS AND FUTURE STUDIES</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td>ACKNOWLEDGEMENTS</td>
<td>v</td>
</tr>
</tbody>
</table>
CHAPTER 1

INTRODUCTION
Thin films of compound semiconductors have been used as materials for the fabrication of electronic and optoelectronic devices, such as transistors, lasers, detectors, light-emitting diodes (LEDs), displays, thermoelectrics, and photovoltaics [1-6]. The films with crystalline structure are generally grown on well-ordered substrates. The properties of deposited films are altered by accurately controlling composition, dopant, and structure. Epitaxy, a desirable property of deposits, is defined here as the formation of crystalline solid deposits whose structure is the same as the substrate [7]. It is generally preferred because epitaxially deposited films tend to have superior quality suitable for electronic and optoelectronic applications. When deposit and substrate are identical in chemical composition, the deposition process is known as homoepitaxy, for example, GaAs deposited on GaAs substrate. In contrast, heteroepitaxy is used when a solid deposit is chemically different from the substrate, such as the growth of CdSe on a InP substrate. Presently, both conventional and non-conventional deposition methods have been used to grow compound semiconductors. The detailed descriptions of these methods are briefly explained in the following sections.

Molecular beam epitaxy (MBE) is conventionally used to form solid deposits of compound semiconductor, especially of the III-V group [8-14]. Depositions are carried out in an ultra high vacuum (UHV) chamber. Pure elements (solid or liquid), contained in crucibles, are constantly heated to produce elemental vapors beams. The beams of atoms or molecules are directly impinged onto an atomically flat substrate, held at a high temperature. The elements are then condensed on the substrate, resulting in an epitaxial deposit. Depositions are primarily controlled by temperatures and the rates of elements arriving at the substrate, fluxes. Excess elemental vapor can condense at the wall of the deposition chamber, kept at liquid nitrogen temperature, and thus eliminated out from the system. The growth rate of a deposit is very low,
about one atomic layer per second. This allows enough time for the elements to diffuse to stable lattice site on the substrate. Each elemental source is generally equipped with a beam shutter that can be opened or closed in a matter of seconds. The composition and incorporation of a dopant can be abruptly varied by switching from one source to another. Thus, multilayer and heterostructure deposits can be easily formed. The advantages of MBE are that crystalline deposits are epitaxially formed with precise control on composition, dopant, structure, and uniform thickness. In addition, these deposits are performed in an extremely clean environment, and the amount of contaminants is controlled at minimum. However, MBE required a UHV system and other complex instrumentation, resulting in high production costs.

Chemical vapor deposition (CVD) is another conventional deposition method for compound semiconductors used in electronic devices and integrated circuits [15-18]. It can be operated near atmospheric pressure. Gaseous precursors are transported into a reaction chamber via a carrier gas. A deposit is formed by a chemical reaction of the gaseous precursors on or near a heated substrate. A number of chemical reactions are used in CVD method, such as thermal decomposition (pyrolysis), reduction, oxidation, hydrolysis, carburization, nitridization, and disproportionation. These reactions are activated by using temperature, plasma, and electromagnetic radiation. Metalorganic chemical vapor deposition (MOCVD), an important variant of CVD, is widely used to deposit epitaxial films of compound semiconductors of the III-V and II-VI groups [19]. The precursors are metalorganic compounds, which contain atoms of desired element bound to organic species. Epitaxial deposits are formed through the decomposition of mealorganic precursors. For example, GaAs can be obtained from Ga(CH₃)₃ and AsH₃ precursors. The deposition temperature is much lower than that used in conventional CVD because metal-organic compounds are very reactive. Thus, interlayer diffusion of elements
is less likely to occur, and deposits with sharp heterojuctions can be easily formed. However, the metalorganic vapors are very toxic and have high vapor pressures at room temperature. Extreme caution must be exercised in the workplace because life-threatening doses of AsH₃ and PH₃ are 6-15 and 400-600 ppm, respectively, for a period of 30-60 s.

Atomic layer epitaxy (ALE) is a gas or vacuum-phase deposition method used to deposit thin films of compound semiconductors of II-VI group, III-V group, oxides, and nitrides for applications in electronics, optics, and catalysis [20-24]. It was first invented by Suntola and Antson. ALE uses surface-limited reaction to precisely control the growth of a deposit, at one atomic layer at a time. An ALE cycle consists of three steps: precursor chemisorption, surface reaction, and desorption. For example, in the case of ZnS deposition, ZnCl₂ gas was flowed over a substrate (glass or Corning 7059), terminated with oxygen atoms. One monolayer of ZnCl₂ adsorbed on the substrate surface through bonding between ZnCl₂ and O atoms. A carrier gas was used to eliminate extra ZnCl₂. Then, H₂S gas was flowed in. The reaction between adsorbed ZnCl₂ and H₂S resulted in an atomic layer of ZnS and HCl gas, diffusing away from the substrate. The thickness of deposit depends on the number of deposition cycles.

Electrodeposition is an alternative method for preparation of compound semiconductors [25-27]. It is considerably less expensive than conventional method because the deposition can be performed under ambient conditions, and no sophisticated deposition system is required. The precursor ions are mainly inorganic salts, which are generally less toxic than the precursors used in MBE and CVD. Deposit can be grown uniformly on an irregular-shaped substrate. The conventional electrochemical method, co-deposition, is commonly used to grow films of compound semiconductors, especially metal chalcogenides. Kroger et al. first reported CdTe deposition by co-deposition [28]. Precursor ions (Cd²⁺ and Te⁴⁺) were contained in a single
deposition bath. Deposition was carried out under potentiostatic control. Although the co-deposition method is very simple, it is difficult to control both composition and structure of as-deposited films. Post-deposition annealing at high temperatures under inert atmosphere is normally used to improve the film properties.

Electrochemical atomic layer epitaxy (EC-ALE) has been developed in this research laboratory, and others, to prepare thin films of various compound semiconductors [29-52]. It is based on atomic layer epitaxy (ALE) [20-24] where deposits are grown layer-by-layer. Surface-limited reactions, referred to as underpotential deposition (UPD), are used to limit deposition of an element to one atomic layer at a time. A monolayer (ML) is defined here as a ratio of adsorbate to electrode surface atoms. For example, if one full ML of Cd is deposited on an ideal Au(111) electrode (1 cm²), the number of Cd atoms is equal to $1.35 \times 10^{15}$ atoms Cd. UPD is an electrochemical reaction where an element is deposited at a potential prior to that required to deposit the element on itself [53-55]. The reaction proceeds as a result of the free energy gained from compound formation between element and surface atoms. In principle, EC-ALE promotes two-dimensional deposit growth and offers better control over composition, structure, and morphology than conventional electrodeposition methods, such as co-deposition. An EC-ALE cycle consists of a sequence of deposition steps, where constituent elements, forming a compound, are deposited at UPD potentials. Each step can be individually optimized to grow just one atomic layer at a time. The deposition cycle can be repeated as needed to form films of a certain thickness.

An electrochemical quartz crystal microbalance (EQCM) is an electroanalytical method, which is capable of measuring minute mass changes on its surface while providing conventional electrochemical data in the same time. The theory and applications of EQCM have been
reported in literatures [56-63]. In 1880, the Curie brothers discovered the piezoelectric effect in various crystals (quartz, rochelle salt, and tourmaline) [64]. Later on, they showed that converse piezoelectric effect also existed. The phenomenon was observed when an electrical potential was applied across the crystals, mechanical stress was induced. The principle operation of an EQCM is based on the converse piezoelectric effect. According to the crystal symmetry of quartz, a mechanical stress induced by one polarity of electrical potential is equal in magnitude, but opposite in direction to the mechanical stress induced by the opposite polarity of electrical potential. The application of the alternating electrical potential to a crystal surface results in atomic displacement of the crystal in the shear mode, whose oscillation amplitude is parallel to the crystal surface. The shear vibration establishes a transverse acoustic wave traveling back and forth across the quartz crystal. When acoustic wavelength is equal to twice of quartz crystal thickness, a standing acoustic wave condition is satisfied. Thus, the frequency of the acoustic wave in the condition is shown in Eq. 1.1.

\[
\frac{f_o}{2t_q} = \frac{\sqrt{\mu}}{2t_q \sqrt{\rho}}
\]  

(1.1)

where \(f_o\) is the frequency of the quartz crystal (Hz), \(v_{tr}\) is the transverse velocity of sound in AT-cut quartz \((3.34 \times 10^4 \text{ m s}^{-1})\), \(t_q\) is the thickness of the quartz crystal, \(\mu\) is the shear modulus of quartz \((2.947 \times 10^{11} \text{ g cm}^{-1} \text{ s}^{-2})\), and \(\rho\) is the density of quartz \((2.648 \text{ g cm}^{-3})\).

If a rigid film is uniformly attached on a quartz surface, the transverse acoustic wave should continuously propagate through the interface, including the film thickness. A no-slip condition is assumed at the quartz-film interface such that both quartz and film synchronously
undergo particle displacement in a shear mode. In addition, the acoustic properties in quartz and
film are assumed to be identical. Therefore, the apparent thickness of a quartz crystal is equal to
the total thickness of the quartz crystal and any film. Thus, a small change (Δt) in film thickness
causes a small change in frequency of the quartz crystal. Substituting Eq. 1.1 into Eq. 1.2 gives
the Sauerbrey equation [65], Eq. 1.3, demonstrating that frequency changes in a quartz crystal
are linearly proportional to mass changes on the crystal surface.

\[ \frac{\Delta f}{f_o} = \frac{\Delta t}{t_q} = -\frac{2f_o \Delta t}{v_{tr}} \]  

(1.2)

\[ \Delta f = \frac{2f_o^2}{\sqrt{\mu \rho}} \Delta m = -C_f \Delta m \]  

(1.3)

where Δf is the frequency change (Hz), Δm is the mass change per unit area (g cm\(^{-2}\)), A is the
piezoelectrically active area (cm\(^2\)), Δt is equal to Δm/Aρ, and C\(_f\) (Hz cm\(^2\) g\(^{-1}\)) is the sensitivity
factor. The Sauerbrey equation can be used to determine mass changes on the quartz crystal
when the mass of added film is not more than 2 % of the mass of the crystal.

When a QCM is used in a solution phase, the oscillation of the quartz crystal is damped
because of the extra weight and viscosity of solution in contact with the surface. Calibration of
an EQCM is required to accurately convert measured frequency changes to mass changes. Metal
electrodeposition (Ag, Cu, and Pb) is generally used to calibrate an EQCM in a liquid, as 100 %
efficiency for the faradaic process can be assumed. A plot of Δf vs. Q is linear, and a C\(_f\) value
can be calculated from the slope.
This dissertation describes the application of a flow cell EQCM to studies of the electrodeposition of binary compound semiconductors using EC-ALE. The construction of the flow cell EQCM was described in chapter 2. Two pumping methods (Helium pressure and peristaltic pump) were used to deliver solutions to the cell with acceptable $\Delta f$ fluctuations. The effect of solution flow on $\Delta f$ measurements was also reported.

A wide variety of thin films of compound semiconductors have been grown via EC-ALE, such as ZnSe [36], Cd chalcogenides [43, 50, 66, 67], PbS [49], PbSe [68], InAs [69], InAs/InSb [70], In$_2$Se$_3$ [71], and Bi$_2$S$_3$ [48]. Film composition is initially approximated by measuring charges passed during deposition. In case of CdSe, precursor ions (Cd$^{2+}$ and Se$^{4+}$) were used to deposit atomic layers of Cd and Se. If stoichiometric CdSe is deposited, charges passed during the Cd step would be half of those for Se, as Cd$^{2+}$ and Se$^{4+}$ undergo reduction via two and four-electron processes, respectively.

When films were grown via EC-ALE, the coulometric analysis suggested that the films were non-stoichiometric. However, subsequent electron probe microanalysis (EPMA) investigations indicated that the films were stoichiometric. Extra charges may correspond to side reactions, such as hydrogen evolution and oxygen reduction, that can occur during film growths. These reactions would cause errors in film composition calculated from coulometry.

To investigate the origins of such problems, the flow cell EQCM was used to deposit binary compound semiconductors on a Au-coated quartz crystal. A series of depositions for CdSe and PbTe were carried out using various deposition programs. Cyclic voltammetry was used to determine both UPD and bulk deposition potentials for the elements on a Au electrode. Both current and $\Delta f$ were simultaneously measured as a function of the deposition time and used
to calculate coverages of the depositing elements. The calculated coverages were compared.

These results facilitated determination of optimized deposition conditions for CdSe and PbTe.

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CHAPTER 2

FLOW CELL ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE (EQCM) FOR ELECTRODEPOSITION OF COMPOUND SEMICONDUCTORS VIA EC-ALE

1Srisook, N. and J.L. Stickney. To be submitted to Analytical Chemistry.
Abstract

A flow cell electrochemical quartz crystal microbalance (EQCM) is reported here. It has been designed for studies of the formation of compound semiconductors using electrochemical atomic layer epitaxy (EC-ALE) method. The flow cell was modified from previous flow cell designs to fit the small size of a 9-MHz EQCM crystal. Helium pressure was used to push solutions through the deposition cell, with a minimal noise level in frequency change (Δf) measurements. Peristaltic pumps were also examined, and found to work acceptably, although some increases in Δf fluctuations were observed, relative to pressure flow. When solution flow was stopped, shifts in Δf were observed, with magnitudes dependent on the initial flow rate. Calibration of the EQCM was carried out using Ag electrodeposition combined with cyclic voltammetry. PbSe was deposited on a Au-coated quartz crystal. Coverages calculated from charges and Δf were compared, with differences attributed to oxygen reduction. Current-time traces, along with changes in Δf were presented for the initial cycles in the deposition of PbSe using EC-ALE.

Introduction

A quartz crystal microbalance (QCM) is a mass-sensing device, capable of measuring mass changes equivalent to the formation of a monolayer. The QCM is based on the converse piezoelectric effect, discovered by Curie brothers, where a mechanical stress in a quartz crystal is induced upon the application of an electrical potential [1]. The QCM is composed of a thin quartz wafer sandwiched between two metal disks, attached to an oscillator circuit. AT-cut quartz crystals are commonly used because of their frequency stability as a function of temperature. When an alternating potential is applied perpendicular to the crystal surface, a shear stress is induced in the crystal, and the atomic displacement of quartz occurs in the
direction parallel to its surface. The shear vibration results in acoustic waves traveling perpendicular to the surface. When extra mass is uniformly added on top of the quartz crystal, the thickness of the quartz crystal changes, and a change in the resonance frequency is observed. If the added mass is less than 2% of the mass of the quartz crystal, the relationship between $\Delta f$ and mass change is linear, and described by the Sauerbrey equation [2]:

$$\Delta f = \frac{2n f_o^2}{\sqrt{\mu \rho}} \Delta m = -C_f \Delta m$$

$\Delta f$ is the measured frequency change (Hz), $f_o$ is the resonance frequency of the quartz crystal (Hz), $\Delta m$ is the change in mass per unit area (g cm$^{-2}$), $\rho$ (2.648 g cm$^{-3}$) is the density of quartz, $\mu$ (2.947 $\times$ 10$^{11}$ g cm$^{-1}$ s$^{-2}$) is the shear modulus of quartz, $n$ is the number of the harmonic at which the crystal is driven, and $C_f$ is the sensitivity factor (Hz cm$^2$ g$^{-1}$) [3]. The negative sign in the Sauerbrey equation indicates that $\Delta f$ decreases when mass is added to a QCM electrode and vice versa. QCM is conventionally used to monitor metal deposition rates in gas phase and in vacuum. Due to its high sensitivity, the use of QCM is steadily increasing, finding uses in immunosensors, DNA-based biosensors, and others applications [4-10]. The history and early applications of QCM can be found in the excellent book by Lu and Czanderna [11].

Early on, it was believed that the QCM could not be used in a solution because the energy loss would be too large and the quartz crystal would cease to oscillate [12]. Preliminary work by Konash and Bastiaans showed that the oscillations of the quartz crystal were stable only when one side of the crystal was in contact with solution [13]. Nomura et al. were the first to successfully use the QCM to measure mass changes, associated with the electrodeposition of Ag.
Bruckenstein et al. also reported the use of QCM to monitor mass changes due to the electrodeposition of Pb and Ag in acetonitrile solution [15]. Later, Schumacher et al. showed that electrochemical oxidation/reduction cycles of a metal electrode resulted in a rougher surface, and extra mass change between cycles was observed because of oxygen and trapped liquid on the rough surface [16]. Since these pioneering works, the use of QCM in electrochemical system has greatly increased [17, 18]. The QCM, working as an electrode, provides mass information in addition to electrochemical data, allowing electrochemists to study more complex systems. In electrochemical systems, there are two basic types of reactions: faradaic and non-faradaic. The former is a charge-transfer reaction; an electron is transferred across the solution-electrode interface. The latter occurs without electrons being transferred, but may involve the adsorption of electrolyte on an electrode. The results can be interpreted given knowledge of all electroactive species involved. In the case of non-faradaic reactions, it is generally not enough to rely on electrochemical data alone. Using a QCM, if electrolyte adsorption occurs, an increase in mass is expected, and can be detected by a change in the resonance frequency. From here on, the term EQCM will be used when the subject of study is an electrochemical process. The theory and applications of EQCM have been previously reviewed [1, 3, 19-24].

Electrochemical atomic layer epitaxy (EC-ALE) has been developed and used to form thin films of compound semiconductors [25-29]. It is based on atomic layer epitaxy (ALE) where the constituent elements of a compound are deposited alternately layer-by-layer, using surface-limited reactions [30-32]. Surface-limited reactions in electrochemistry are generally referred to as underpotential deposition (UPD). UPD is an electrochemical reaction where one element is deposited on a second element, at a potential prior to that required to deposit the element on itself [33-36]. The reaction proceeds as the result of the free energy change in
forming a surface compound or alloy, between the depositing element and surface atoms. Surface-limited reactions, UPD, are used to limit deposition of an element to an atomic layer at a time. An atomic layer suggests a uniformly grown adsorbate on a substrate, one atom high, but with an indefinite coverage. On the other hand, a monolayer (ML) is defined here as a ratio of the number of adsorbate atoms to the number of adsorbate surface atoms. For example, if one ML of Cd is deposited on a Au(111) electrode, the number of Cd atoms is equal to $1.35 \times 10^{15}$ atoms cm$^{-2}$, equal to the surface atomic density for Au(111). EC-ALE is the use of UPD in a ALE cycle. The reason for using EC-ALE is that it should promote two-dimensional growth, and offer better control over deposit thickness, composition, structure, and morphology, than conventional electrodeposition methods such as co-deposition [37]. It breaks the whole deposition process down into a series of sequential steps, which can be individually optimized to deposit one monolayer of the compound. An EC-ALE cycle is composed of a sequence of steps wherein atomic layers of the constituent elements in a compound are deposited. The thickness of a film is then controlled by the number of cycles performed.

Thin films of compound semiconductors, including III-V, II-VI, and IV-VI, have been previously grown using EC-ALE [38-45]. Depositions were performed under potential control, and the currents were monitored. Via Faraday’s law, film compositions were calculated from the amount of charges passed during the depositions. Thus, the stoichiometries of deposits were determined directly from the charges measured. For instance, when a CdTe film was deposited, the charge in a Cd deposition step should be half of the charge measured in the Te deposition step, as Cd$^{2+}$ and Te$^{4+}$ were used as precursors and resulted in two and four electron processes, respectively. However, this frequently was not the case, and the relative charges were frequently not 2:1. On the other hand, after the deposit was formed, electron probe microanalysis (EPMA)
showed the deposits to be stoichiometric. There are a number of possible reasons for these differences, such as charging currents, hydrogen evolution, oxygen reduction, or other trace contaminants. It is also possible that extra Cd may have deposited, and then react with Te$^{4+}$ ion in the Te step, resulting in more charge for Cd and less than expected for Te. This would have been a spontaneous chemical reaction where Te deposited and Cd stripped. To investigate these problems, an EQCM has been constructed to grow deposits using an EC-ALE cycle. This allows mass change measurements during Cd and Te deposition steps, possibly allowing confirmation of the presence of a chemical reaction between Cd and Te$^{4+}$. At the same time, conventional electrochemical data (potentials, currents, and charges) would be measured. The deposited amounts can then be calculated from the two data sets and compared. The difference, if any, will help in understandings the formation of compound semiconductor by the EC-ALE method.

In the EC-ALE deposition method, precursor ions for each element are contained in separated optimized solutions. The solutions are rinsed into the deposition cell under potential control, and deposition occurs under potential control. A blank solution is used to rinse out electroactive species from step to step, to prevent mixing between precursor solutions and the co-deposition, which could result. A flow cell is used to facilitate the solution exchange. The depositions can then be continuously monitored.

This paper describes the construction of a flow cell EQCM to study compound semiconductor formation using the EC-ALE method. The cell design was modified from the flow cell currently used in our laboratory to accommodate the smaller size of the EQCM electrode. Two pumping methods were tested, to investigate solution flow problems and noise levels. The effects of solution flow on $\Delta f$ measurements were also reported. The application of the flow cell EQCM to the growth of PbSe was demonstrated.
Experimental

Conventional holders for EQCM are generally made of chemically inert materials (Teflon) [46]. There are two basic types: dip and well. In the case of the dip holder, the cell is immersed into a solution, and the exposed face is used as a simple planar electrode with semi-infinite boundary conditions. With the well holder, a column of solution is held above or on the side of the electrode with similar results to the dip holder. In both cases, the holder maintains one side of the EQCM, exposed to air, while the other is in contact with electrolyte. Using EQCM, electrochemical data and frequency (mass) changes are simultaneously monitored and compared. The results help many investigators to study complex electrochemical systems, such as electronstic valency of metal deposition and anion adsorption. Although the setup is very simple and easy to use, it only works for one solution at a time.

There have been several reports on flow cell designs combined with EQCM [47-56]. In this work, the flow cell EQCM design shown in Figure 2.1.1 and 2.1.2 was used, based on the flow cell currently used in this laboratory [41, 57]. It was modified to accommodate the EQCM electrode, which was much smaller than the Au-on-glass substrate (5 x 2 cm) generally used. Nine MHz AT-cut quartz crystals (Figure 2.2) were purchased from Seiko EG&G. Both sides of the quartz crystal were coated with circular Au electrodes (ca. 0.2 cm², 5 mm in diameter). The electrodes were formed with 50 nm of Ti, followed by 300 nm of sputtered Au. The quartz crystal was cleaned with concentrated sulfuric acid in an ultrasonic bath (Cole-Parmer, Vernon Hills, IL) for two minutes. It was rinsed thoroughly with de-ionized water and carefully blown dry with N₂. The quartz crystal was then sandwiched between two Silicone gaskets (0.081 cm thick) and placed inside the flow cell, comprised of two Plexiglas blocks. Machine screws were used to tighten the flow cell. The Silicone gaskets had circular hole, 7 mm in diameter. One Au
Figure 2.1.1 A diagram for the deposition system consisted of (a) Pyrex bottle, (b) solenoid valve, (c) distribution valve, (d) flow cell EQCM, (e) oscillator unit, (f) frequency counter, (g) potentiostat, (h) interface board for valve control, (i) computer, (j) peristaltic pump, and (k) waste container. The drawing was not to scale.
Figure 2.1.2  Diagrams of the flow cell EQCM showing (a) side view and (b) top view.
Figure 2.2 A Au-coated AT-cut quartz crystal, purchased from Seiko EG&G. The fundamental resonance frequency was 9 MHz.
electrode on the quartz crystal was exposed to solution (~20 µL) and served as a working electrode, while the other electrode was open to trapped air. A thin Au wire (Wilkinson Company, Inc., Post Falls, ID), placed at the cell outlet, was used as the auxiliary electrode. All potentials were reported vs. a Ag|AgCl|3 M NaCl reference electrode (Bioanalytical Systems, Inc., West Lafayette, IN). The flow cell and oscillator circuit were housed inside a homemade Faraday cage, held inside a Plexiglas box, to eliminate electrical noise from \( \Delta f \) measurements and exclude oxygen, respectively. Solution containers were housed in a second Plexiglas box, as well. Liquid nitrogen blow off was used to purge the Plexiglas boxes while He gas (99.99 %) was used to purge all solutions. An oxygen analyzer (Illinois Instruments Inc., Johnsburg, IL) was used to measure the residual O\(_2\) level, typically \( \sim 15 \) ppm, from the gas outlet. Solutions were delivered through a Teflon distribution valve to the cell, using the pressure method or a peristaltic pump (Cole-Parmer, Vernon Hills, IL). When the pressure method was used, an adjustable micro-metering valve (Upchurch Scientific, Oak Harbor, WA) was placed at the cell inlet, to control solution flow.

A Seiko EG&G quartz crystal analyzer (Model QCA917) was used to measure \( \Delta f \), with a sample period of 0.1 s. The standard frequency change on the counter was reset to zero before recording was initiated. An EG&G potentiostat (Model 263A) was used to control applied potentials and measure current. Data acquisition for cyclic voltammetry and chronoamperometry was performed with PowerCV and PowerSTEP software (EG&G). A Pentium-based computer, equipped with a PCLD-812PG interface board (Advantech, Irvine, CA), was used to control valves and potential. The deposition program was written in LabView 4.0 (National Instruments, Austin, TX). AgNO\(_3\) and HClO\(_4\) were analytical grade or better. The Pb(ClO\(_4\))\(_2\) (Aldrich) concentration was 0.2 mM, pH 5.5, with 50 mM CH\(_3\)COONa.3H\(_2\)O (J.T.Baker). The SeO\(_2\)
(Aldrich) concentration was 0.2 mM, pH 5.5, with 50 mM CH$_3$COONa.3H$_2$O. The blank solution, pH 5.5, was used to rinse electroactive species out of the deposition cell. The supporting electrolyte was 0.1 M NaClO$_4$ (Alfa Aesar). De-ionized water (18.0 MΩ cm), obtained from a NANOpure UV ultrapure water system (Barnstead International, Dubuque, IA), was used for all solutions.

**Results and Discussion**

When the EQCM was used to study electrochemical process, only one side of the quartz crystal was in contact with solution. The resonance frequency of the quartz crystal decreased from its original value by ~2 kHz upon immersion, because of the interaction of the vibrating crystal and the solution. The sensitivity factor in solution cannot be calculated accurately from Sauerbrey equation. Thus, calibration was required in order to relate frequency changes to mass changes for the EQCM operating in solution. There have been several reports on EQCM calibration [58-62]. In the present study, the EQCM was calibrated via Ag electrodeposition, combined with cyclic voltammetry. Figure 2.3 shows a cyclic voltammogram and corresponding Δf in 2 mM AgNO$_3$, 0.1 M HClO$_4$, on a Au-coated quartz crystal, under static condition (no solution flow). When the potential was scanned in the negative direction from +0.85 V, cathodic current starts to increase at +0.45 V. A small shoulder and a broad peak are observed. When the potential is reversed at –0.10 V, cathodic current is still observed, and diffusion-limited Ag electrodeposition is evident. The overall Δf was –2.082 kHz. In the potential range of +0.32 to +0.79 V, the anodic peak and corresponding Δf are attributable to Ag oxidation. Charges for both the reduction and oxidation processes were plotted against measured values of Δf. The Δf-Q graphs were linear as shown in Figure 2.4, and from the slopes, an average calibration constant of 5.00 ng cm$^{-2}$ Hz$^{-1}$ was determined.
Figure 2.3  Cyclic voltammogram on a Au-coated AT-cut quartz crystal and corresponding Δf in a solution containing 2 mM AgNO₃ and 0.1 M HClO₄ under static condition. The scan rate was 5.0 mV s⁻¹.
E/V vs. Ag|AgCl|3 M NaCl

I/µA

Δf/kHz
Figure 2.4  Δf-Q plots for (a) electrodeposition and (b) electrodissolution of Ag from a Au-coated quartz crystal in a solution containing 2 mM AgNO₃ and 0.1 M HClO₄ under static condition.
Slope = 1.132 kHz mC$^{-1}$
Slope = 1.102 kHz mC$^{-1}$
There was a significant learning curve for using the flow cell EQCM. Most of the issues to be discussed here involved the effect of solution flow on $\Delta f$ measurements. It was important to determine the noise level in the $\Delta f$ measurements associated with flowing solution, relative to static conditions (used as a reference point). An HClO$_4$ solution was used, as perchlorate ions are known to adsorb only weakly on Au [63], and HClO$_4$ is available in high purity. The EQCM cell was first filled with 0.1 M HClO$_4$ solution, and a scan was initiated after the solution flow was stopped for 10 minutes. Figure 2.5(a) shows $\Delta f$ curve at +0.20 V in 0.1 M HClO$_4$ under static conditions. The $\Delta f$ was stable over the recording time. There was no significant fluctuation or drift observed. The noise level in the $\Delta f$ measurement was determined by calculating the standard deviation. The result was 0.20 Hz. If Cd were deposited with such a noise level, an error in the Cd coverage would be about 0.0034 ML.

To flow solutions, the pressure method was used first, where a positive pressure of helium forced solutions from the Pyrex bottles through the EQCM cell. All solution bottles were closed with Teflon caps, which had three 1/4"-28 tapped outlets: for the solution, He gas in, and the vent as shown in Figure 2.1.1. Stainless springs were used to secure the Teflon caps in place. Helium was used instead of the less expensive N$_2$ because of its lower solubility in the aqueous solutions. Under room temperature and atmospheric pressure, the mole fraction solubility of He in an aqueous solution is $6.997 \times 10^{-6}$, compared to that of N$_2$ ($1.183 \times 10^{-5}$) [64]. When N$_2$ was used, bubbles slowly formed inside the cell volume, visible after 5 minutes of flowing solution through the cell. The trapped bubbles resulted in a significant increase in frequency fluctuation, not related to mass change on the electrode, resulting in errors in the interpretation of frequency changes. Bubble formation appears to result from N$_2$ leaving solution, due to small pressure changes upon entering the cell, as solutions are flowed from the pressurized bottle to the
Figure 2.5 A series of $\Delta f$ measurements as a function of time at the applied potential of $+0.20$ V with the flow rates of (a) 0.0, (b) 0.060 (He pressure), (c) 0.12 (He pressure), (d) 0.31 (peristaltic pump) mL min$^{-1}$. The solution was 0.1 M HClO$_4$. 
deposition cell, which is opened to atmosphere through the outlet. The lower solubility of He appears to avoid these problems. Figure 2.5(b)-(c) shows $\Delta f$ curves as a function of time at $+0.20$ V in 0.1 M HClO$_4$ under solution flow rates of 0.060 and 0.12 mL min$^{-1}$, using He. The standard deviations in Figure 2.5(b)-(c) were calculated as 0.18 Hz (0.0031 ML Cd) and 0.28 Hz (0.0048 ML Cd). At the lower flow rate, the stability of $\Delta f$ was excellent and comparable to that under static conditions, Figure 2.5(a). At 0.12 mL min$^{-1}$ flow rate, fluctuations were still quite low, but some small pulsing in the $\Delta f$ measurement was evident. Apparently, flow rates of 0.060 mL min$^{-1}$ or lower minimize noise. Using the pressure method, however, there was a significant dead volume, between the distribution valve and the cell inlet, due to the valving, it thus took a long time to flow solution into the cell. To decrease solution exchange times, a flow rate of 0.50 mL min$^{-1}$ was used instead. Although the pressure method gave stable $\Delta f$ measurement when solutions were flowed continuously, some parameters were found to affect the $\Delta f$, without any mass change on the surface. For example, when switching between two solutions, small shifts in $\Delta f$ were observed. This appeared to be due to small difference in the flow rates, resulting from variations of solution levels in the pressurized bottles and tubing lengths.

To cut down the rinsing time, a six-roller peristaltic pump with a variable speed control was used to pump solution to the EQCM cell. The pump was simple to operate and provided a constant flow rate over a long period of time. It was also convenient to change the flow rate by either adjusting the rotation speed of the pump or changing the ID of the Tygon tube. The pump was connected at the cell outlet as shown in Figure 2.1.1 so that the pumping sucked the solution from bottles through the cell. Only one pump was required, and the dead volume between the distribution valve and the cell was minimized by using PEEK tube (0.0762 cm ID). If solutions were pushed through the deposition cell, several pumps would be needed, one for each solution
used in a system. Figure 2.5(d) shows the $\Delta f$ curve at $+0.20$ V in 0.1 M HClO$_4$ under a flow rate of 0.31 mL min$^{-1}$ using the peristaltic pump on the outlet. The cell volume was ~20 $\mu$L and the dead volume between the cell and the selection valve was ~0.2 mL. The $\Delta f$ measurement showed some pulsing and fluctuation. The standard deviation, 0.56 Hz (0.0096 ML Cd), was close to the standard deviation calculated from the static condition. The $\Delta f$ instability was random, contributing less than 0.01 ML Cd of uncertainty. It is possible to reduce the noise level further by using a 12-roller peristaltic pump, or a pulse-damping device, placed between the cell outlet and the peristaltic pump.

The electrodeposition of compound semiconductors using the EC-ALE method is generally done using stop-flow conditions, in this group. A precursor ion solution was pumped into the deposition cell for a short time, and the pump stopped. Deposition proceeded at a controlled potential under static condition for about 20 s. Then, a blank solution (no electroactive ion) was pumped into the cell to rinse out the previous solution. It was thus desirable to use the same program for the EQCM experiments. To study the effect of stop flow on $\Delta f$ measurements, a series of $\Delta f$ curves in 0.1 M HClO$_4$ at $+0.20$ V with solution flow rates of (a) 0.049, (b) 0.17, and (c) 0.43 mL min$^{-1}$ were run (Figure 2.6). The solution was continuously flowed through the cell using the pressure method, and $\Delta f$ was simultaneously monitored. Then, the solution flow was stopped after 100 s, until the end of the scan. No significant fluctuation or drift observed in the initial 100 s. When the solution flow was stopped, shifts in $\Delta f$ were observed in all three scans. The magnitude of the shift was dependent on the solution flow rate used. In Figure 2.6(a), a small shift was observed, which stabilized after 15 s. In Figure 2.6(b) and (c), $\Delta f$ did not stabilize over 400 s. Furtado and Thompson studied the hybridization of oligonucleotides using QCM under stop-flow conditions [65]. They used solution flow rates of
Figure 2.6 A series of $\Delta f$ measurements as a function of time at the applied potential of +0.20 V with the flow rates of (a) 0.049, (b) 0.17, and (c) 0.43 mL min$^{-1}$ before the solution flow was stopped at 100 second until the end of scan. Helium pressure was used to push solution through the deposition cell. The solution was 0.1 M HClO$_4$. 
0.074 mL min\(^{-1}\) and were able to monitor \(\Delta f\) without observing any shift when the solution flow was stopped. Másson et al. used a QCM as a bioaffinity sensor for biotin under stop-flow condition, at a flow rate of 1.5 mL min\(^{-1}\) [66]. Solution was injected to the cell for 3 mins, and the pump was stopped. The frequency of QCM was recorded 20 mins after the start of the injection. They also noted that under the stop-flow condition the frequency was not stabilized over a period of 1 hour after the pumping was stopped.

When solutions were flowed through the cell, there was a change in pressure. Ideally, this should not result in a change in frequency. However, given the design of the flow cell, and the gaskets used, frequency changes were observed with these changes in pressure. The effect of pressure on \(\Delta f\) measurement was reported by Heusler and co-workers [67]. When solution flow was stopped, it is also possible that there are changes in stress on the crystal. Changes in pressure result in changes in stress via the gaskets, which hold the crystal, and thus changes in frequency. Another possible reason for the frequency changes is hydrodynamic coupling. It is known that a thin layer of solution next to the crystal surface vibrates (oscillates) synchronously with the oscillating motion of the quartz crystal [22]. When solution flow is stopped, the vibrating motion of the solution changes, resulting in the observed \(\Delta f\) shift. However, it is not clear how such coupling could take so long to change, 400 sec. From previous studies and these results, it is clear that the EQCM can be used under stop-flow mode only if a solution flow rate of about 70 \(\mu\)L min\(^{-1}\) or lower is used to avoid \(\Delta f\) shifts. More research is needed to explain the origin of the shift in \(\Delta f\). Presently, to avoid these problems, continuous flow is being used.

Figure 2.7 shows current and \(\Delta f\) results for the deposition of 5-cycle PbSe via the EC-ALE method. The solutions were continuously delivered to the deposition cell at the flow rate of 0.50 mL min\(^{-1}\). An atomic layer of Pb was deposited first, followed by Se. The deposition
Figure 2.7  Current and $\Delta f$ traces for the deposition of PbSe (5 cycles) via EC-ALE. The deposition potential was $-0.40 \text{ V}$. The solutions flow rate was 0.50 mL min$^{-1}$. 
potential was kept constant at –0.40 V. The coverages of Pb and Se, for each cycle, were
calculated as shown in Figure 2.8. In the first cycle, both Pb and Se coverages calculated from
the charges were larger than those calculated from $\Delta f$. The extra charge corresponded to trace
oxygen dissolved in the deposition solutions. From the 2nd to 5th cycles, the Se coverages
calculated from coulometry were approximately the same as those calculated from $\Delta f$. Plots of
charges vs. $\Delta f$ were linear. For Se deposition, the slope value, $M/z$, was 17.0 g equivalent$^{-1}$, very
close to the theoretical value (19.7 g equivalent$^{-1}$). In the case of Pb, extra charge was observed
from the 2nd through 5th cycles, and the Pb coverages were larger than those calculated from $\Delta f$.
It has been reported in the literatures that oxygen reduction is catalyzed by the presence of Pb
UPD [68, 69]. This explains the extra charges observed in the Pb deposition step. Overall, it
was shown that the flow cell EQCM could be used to measure the amounts of Pb and Se
deposited via EC-ALE. From the $\Delta f$ results, a side reaction, oxygen reaction, was identified. It
should be noted here that the results on PbSe deposition via EC-ALE were preliminary.
Additional studies have been initiated to obtain an optimized deposition program for the growth
of PbSe. In summary, the use of EQCM allows the mass actually deposited on the electrode to
be determined. Comparisons between mass changes and charges can be used to better
understand the surface chemistry during the EC-ALE cycle.

**Conclusions**

In these studies a flow cell EQCM was constructed for studies of compound
semiconductor formation using EC-ALE. The cell design was modified from the flow cells
currently used in this laboratory. High purity He was used to purge solutions instead of nitrogen
gas to avoid trapping bubbles inside the cell volume. Two pumping methods (He pressure and
peristaltic pump) were used to flow solutions through the cell. Solution flow rate up to 0.50 mL
Figure 2.8  Plots of calculated coverages as a function of deposition cycles: (□) Pb, charge; (■) Pb, Δf; (○) Se, charge; and (●) Se, Δf.
min$^{-1}$ were used with minimal noise in $\Delta f$ measurements. The effects of solution flow rates on frequency change were also studied. When solution flow was stopped, shifts in $\Delta f$ were observed, with the magnitude dependent on the solution flow rate. It appears these were due to changes in pressure in the deposition cell. Flow rates as low as 70 $\mu$L min$^{-1}$ were required to avoid significant $\Delta f$ shifts. The flow cell EQCM was used to grow 5 cycles of PbSe using an EC-ALE cycle. The coverages calculated from coulometry were higher than those calculated from $\Delta f$, apparently due to reduction of trace oxygen dissolved in the deposition solutions. From $\Delta f$ results, coverages of Pb and Se were 0.4 and 0.3 ML, respectively.

References

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CHAPTER 3

FLOW CELL ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE (EQCM)

STUDIES FOR THE ELECTRODEPOSITION OF CDSE VIA EC-ALE\(^1\)

\(^1\)Srisook, N. and J.L. Stickney. To be submitted to *Journal of The Electrochemical Society*. 
Abstract

Binay Cd chalcogenide compound semiconductors (CdS, CdSe, and CdTe) are important materials for optoelectronic applications, such as blue/green lasers and photovoltaics. A flow cell electrochemical quartz crystal microbalance (EQCM) was used to study CdSe deposition via electrochemical atomic layer epitaxy (EC-ALE). It is the electrochemical analog of atomic layer epitaxy (ALE). ALE is based on the use of surface-limited reactions to form compounds one atomic layer at a time. Electrochemical surface limited reactions, referred to as underpotential deposition (UPD), are used to deposit atomic layers of the constituent elements to form a compound in layer-by-layer. EC-ALE allows better control of thin films growth, and control over composition and morphology, resulting in higher quality films. Cyclic voltammetry was used to determine potentials for UPD of both Cd and Se. The effect of potential shifts to the growth of CdSe on CdSe-covered Au electrode was carried out. The results confirmed that potential shifts from cycle to cycle were required in the formation of CdSe, as has been observed in the EC-ALE formation of other compound semiconductors. A variety of potential programs were used to form 40-cycle deposits of CdSe on a bare Au electrode. Current and Δf data were recorded simultaneously, as a function of the deposition time. Coverages were calculated and reported vs. one full ML of zinc blende CdSe on Au(111). Deposition conditions suitable for the formation of CdSe via EC-ALE were determined.

Introduction

II-VI compound semiconductors have received much interest as materials for the fabrication of optoelectronic devices, such as infrared lasers, blue-green lasers, infrared detectors, light-emitting diodes (LEDs), and photovoltaics [1]. Conventional methods for deposition of compound semiconductors include molecular beam epitaxy (MBE) [2-8] and
chemical vapor deposition (CVD) [9-11]. Such depositions are generally carried out in gas or vacuum phase, using high purity precursors, minimizing contamination and allowing growth of solid-state deposits having electronic-graded quality. However, production cost is high, given the need for sophisticated instrumentation. In MBE and CVD, high temperature is generally used to control the film growth, stimulating interlayer diffusion. In multilayer deposits of two or more compounds, cracking can occur because of differential thermal expansion coefficients, as the deposit is cooled from the deposition temperature to room temperature.

There are alternative deposition methods, such as successive ionic layer adsorption and reaction (SILAR) [12], chemical bath deposition (CBD) [13], and various forms of electrodeposition [14-17]. Among these methods, electrodeposition has received much interest because the production cost for film growth is low, and the deposition system can be easily scaled up for large-area film production. Electrochemical co-deposition, first described by Kroger and co-workers [18], has been primarily used to deposit thin films of II-VI compound semiconductors [16]. A single deposition bath contains ionic precursors for each of the component elements. Films are grown in a single step under potentiostatic or galvanostatic conditions. The use of higher temperatures, limited by the boiling point of the solvent, tends to result in better quality deposits. Although the method is very simple, it is often difficult to control film stoichiometry and morphology at the same time. For example, excess Se was observed in co-deposited CdSe, due to a conproportionation between H$_2$SeO$_3$ and electrochemically generated H$_2$Se [19]. A post-deposition annealing generally improved film stoichiometry and structure, however.

Electrochemical atomic layer epitaxy (EC-ALE) has been developed and used to prepare thin films of compound semiconductors [20-24]. It is based on atomic layer epitaxy (ALE) [25-
where a deposit is grown on a substrate one atomic layer at a time. Electrochemical surface-limited reactions, generally referred to as underpotential deposition (UPD), are used to limit deposition to one atomic layer at a time. UPD is an electrochemical reaction where an element is deposited at a potential prior to the potential required to deposit the element on itself [35-38]. The reaction occurs due to the favorable change in free energy from bonding between an element and the substrate atoms, surface compound formation. EC-ALE promotes two-dimensional growth, and thus, better structure and morphology. The method breaks down the whole electrodeposition process into a sequence of steps, where deposition conditions (solution composition, potential, precursor ion) can be individually optimized for film deposition. An EC-ALE cycle consists of the alternating deposition of constituent elements in a compound using UPD, to produce a compound monolayer. By repeating the cycle, a film of any desired thickness can be grown.

When a compound semiconductor film is grown via EC-ALE, its composition can be estimated from the charges passed during the deposition steps. Faraday’s law allows calculation of deposited amounts. For example, if atomic layers of Cd and Se were deposited on a Au electrode, the reductive charge for the Se step should be twice that of Cd step, because Cd$^{2+}$ and Se$^{4+}$ are used as precursors and undergo two and four-electron processes, respectively. The stoichiometries calculated from coulometry do not always agree with electron probe microanalysis (EPMA) results. Extra charge can originate from background reactions, such as hydrogen evolution, oxygen reduction, charging current, or other contaminants.

A flow cell electrochemical quartz crystal microbalance (EQCM) has been constructed in this laboratory and used to study deposition processes for the formation of compound semiconductors via EC-ALE [39]. EQCM is a mass-sensing device, which is capable of
measuring very small mass changes on a quartz crystal. When mass is deposited on the EQCM electrode, a frequency change is observed. The linear relationship between frequency change and mass change is described by the Sauerbrey equation [40]:

\[ \Delta f = \frac{2nf_o^2 \Delta m}{\sqrt{\mu \rho}} \]

where \( \Delta f \) is the measured frequency change (Hz), \( f_o \) is the resonance frequency of the quartz crystal (Hz), \( \Delta m \) is the change in mass per unit area (g cm\(^{-2}\)), \( \rho \) (2.648 g cm\(^{-3}\)) is the density of quartz, \( \mu \) (2.947 x 10\(^{11}\) g cm\(^{-1}\) s\(^{-2}\)) is the shear modulus of quartz, \( n \) is the number of the harmonic at which the crystal is driven, and \( C_f \) (Hz cm\(^2\) g\(^{-1}\)) is the sensitivity factor [41]. The negative sign in the Sauerbrey equation indicates that \( \Delta f \) decreases when mass is added on the QCM electrode and vice versa.

EQCM has been previously used to study the formation of metal chalcogenides, such as CdSe [42, 43], CdTe [44, 45], ZnTe [46], and Pb chalcogenides [47-50]. This paper describes the application of a flow cell EQCM to studies of the electrodeposition of CdSe using EC-ALE.

**Experimental**

The automated electrochemical deposition system, used to study the deposition of CdSe, has been previously described [39]. It consisted of a flow cell EQCM, a series of solution containers, a distribution valve, a potentiostat, an oscillator unit, and a frequency counter. Deposition solutions were pushed to the deposition cell using pressurized bottles. Helium gas (99.99 %) was used to displace O\(_2\) dissolved in the solutions and build pressures inside the bottles. The deposition system was controlled through a Pentium-based computer equipped with
a PCLD-812PG interface board (Advantech, Irvine, CA). The deposition programs were written in LabView 4.0 (National Instruments, Austin, TX).

The flow cell EQCM consisted of a Au-coated quartz crystal oscillator (working electrode), sandwiched between two Plexiglas blocks with Silicone gaskets. Machine bolts were used to tighten the cell. A thin Au wire (Wilkinson Company, Inc., Post Falls, ID) was used as auxiliary electrode. The reference electrode was Ag|AgCl|3 M NaCl (Bioanalytical Systems, Inc., West Lafayette, IN). Both electrodes were placed at the outlet of the flow cell EQCM to prevent any contaminants of the working electrode. The flow cell EQCM, connected to an oscillator unit (Seiko EG&G, Model: QCA917-11), was housed in a Plexiglas box, and a homemade Faraday cage was used to eliminate electrical interference in $\Delta f$ measurements. A second Plexiglas box was used to house all solution containers. Nitrogen gas (National Welders Supply Co, Charlotte, NC) was used to purge the Plexiglas boxes, producing an oxygen partial pressure below 15 ppm.

AT- cut quartz crystals, purchased from Seiko EG&G, were coated on both sides with evaporated Au (300 nm), on a Ti adhesion layer (50 nm). Before enclosing crystals in the flow cell EQCM, they were cleaned in conc. $\text{H}_2\text{SO}_4$ for five minutes in an ultrasonic cleaner (Cole-Parmer, Vernon Hills, IL). De-ionized water was used to thoroughly rinse the crystals, which were then blown dry with $\text{N}_2$. The crystals were assembled into the flow cell EQCM, described above.

The EQCM was calibrated using Ag electrodeposition and cyclic voltammetry. A cyclic voltammogram was obtained in the potential range of +0.85 to +0.10 V under static conditions (no solution flow). Within this potential range, electrodeposition and electrodissolution of Ag occurs with minimal interference from other reactions, such as Au oxidation and hydrogen
evolution. Thus, the efficiency of the faradaic reactions for Ag were essentially 100%. The integrated current (charges), plotted against measured $\Delta f$ values, resulted in straight lines, and a linear regression analysis was used to fit the data. From the slope values, an average calibration constant was determined to be 5.00 ng cm$^{-2}$ Hz$^{-1}$.

All chemicals were analytical grade or better. The CdSO$_4$ (Aldrich) concentration was 0.5 mM, pH 5.0. The SeO$_2$ (Aldrich) concentration was 0.5 mM, in a pH 5.0 solution. A blank solution, prepared from 50 mM Na$_2$SO$_4$ (J.T.Baker), pH 5.0, was used to rinse electroactive ions out of the deposition cell. The supporting electrolyte was 50 mM Na$_2$SO$_4$ for all deposition solutions. Solution pHs were adjusted with diluted H$_2$SO$_4$ (J.T.Baker). The 10 mM HClO$_4$ (J.T.Baker) was used to clean the electrode before and after depositions. For calibration of the EQCM, a 2 mM AgNO$_3$ in 0.1 M HClO$_4$ was used. De-ionized water (18.0 M$\Omega$ cm), obtained from a NANOpure UV ultrapure water system (Barnstead International, Dubuque, IA), was used to prepare all solutions.

Electrochemical cleaning of the EQCM electrode involved flow of a 10 mM HClO$_4$ solution continuously through the deposition cell at ~0.4 mL min$^{-1}$. The applied potentials were stepped between +1.30 and –0.30 V for three cycles of oxidation and reduction of the electrode. Under constant solution flow, all products (contaminants) were rinsed from the deposition volume, avoiding their re-deposition on the electrode. After cleaning, the blank solution was used to flush the HClO$_4$ from the cell.

Results and Discussion

When an element is electrodeposited, the coverage is reported with respect to the number of surface atoms on the substrate, the Au electrode, the ratio of adsorbate atoms to electrode surface atoms. For example, one ML of Cd on an ideal Au(111) electrode corresponds to 1.35 x
10^{15} \text{ atoms cm}^{-2}. \text{ Although the geometric area of the electrode is known, it is also very important to know the roughness factor for the electrode, to accurately determine the charge corresponding to a ML.}

The total Au electrode area was measured using the oxygen adsorption method [51]. Figure 3.1 shows a cyclic voltammogram and corresponding $\Delta f$ for a Au-coated quartz crystal in contact with the 0.1 M HClO$_4$ solution, under static conditions (no solution flow). When the potential was scanned from +0.40 to +1.00 V, charging current was accompanied by a large $\Delta f$ (–49.0 Hz). The mass increase on the Au electrode corresponds to the adsorption of ClO$_4^-$ ions, reported earlier by Uchida and co-workers [52]. In the potential range of +1.00 and +1.42 V, two anodic peaks, and a small $\Delta f$ (–8.0 Hz), correspond to the oxidation of the Au electrode. At potentials more positive than +1.42 V, the current abruptly increases, the result of O$_2$ evolution. It has been suggested in the literature, that a ML of Au oxide is formed prior to the evolution of oxygen [51]. Thus, the applied potential was limited to below +1.42 V, to form a ML of Au oxide. When the potential was reversed, a cathodic peak, and corresponding $\Delta f$, for reduction of the Au oxide was recorded. The $\Delta f$ values after Au oxide removal correspond to desorption of adsorbed ClO$_4^-$ ions. When the potential was scanned below +0.30 V, the reductive current increased to a plateau at 0.24 $\mu$A, corresponding to reduction of trace oxygen in the solution. At –0.30 V, the observed current was due to hydrogen evolution.

The measured charge (1.294 x 10^{-4} C) under the Au oxide reduction was converted to a number of oxygen atoms using Faraday’s law based on a two-electron reaction. The number of Au surface atoms was then equal to the calculated oxygen atoms. The shapes of the Au oxide peaks in Figure 3.1 are comparable to those reported previously for Au(111) [53, 54]. Thus, it was assumed that the Au electrode used in this present work was predominantly (111) oriented.
Figure 3.1 Cyclic voltammogram and corresponding $\Delta f$ on a Au-coated AT-cut quartz crystal in a solution containing 0.1 M HClO$_4$. The scan rate was 5.0 mV s$^{-1}$. 
Using $1.35 \times 10^{15}$ atoms cm$^{-2}$ for Au(111), the total Au electrode area was calculated to be 0.299 cm$^2$ ($4.038 \times 10^{14}$ atoms) with roughness factor of 1.50, given that the geometric area of the Au electrode was 0.2 cm$^2$.

Cd electrodeposition has been previously reported [55-58]. Figure 3.2 shows a cyclic voltammograms and corresponding $\Delta f$ for a Au-coated quartz crystal in contact with the Cd solution. In the potential range of +0.20 to –0.40 V, two cathodic peaks correspond to Cd UPD, accompanied by a $\Delta f$ of –56.4 Hz. The Cd coverage (0.20 ML) from coulometry was much smaller than that calculated from the measured $\Delta f$ (0.97 ML). It was reported in literatures that $\text{SO}_4^{2-}$ ion co-adsorbed on Cd UPD deposited on the Au electrode [59-61]. Thus, the extra mass is assigned to adsorption of $\text{SO}_4^{2-}$ ions on Cd UPD. When the potential was scanned from –0.40 to –0.60 V, the reductive current and $\Delta f$ were consistent with Cd UPD, corresponding to 0.10 ML. When the potential was scanned further to –0.85 V, the reductive current and $\Delta f$ simultaneously increased and continued even though the potential was reversed for a positive-going scan. The Cd coverage (0.66 ML) calculated from the charges passed was larger than that (0.45 ML) calculated from $\Delta f$ values. The extra charge corresponds to hydrogen evolution, given the acidic solution used in this work. In the potential range, –0.71 to +0.18 V, the anodic current and $\Delta f$ values corresponded to the stripping of Cd UPD and co-adsorbed $\text{SO}_4^{2-}$ ions. At the end of the scan, the $\Delta f$ value did not return to the starting point. The mass increase is assigned to Cd, alloying with Au, which is not completely strip off from the electrode. Cd coverage (0.72 ML) calculated from the oxidative charges was less than that (0.96 ML) calculated from the reductive charges. The difference in coverages confirms the presence of hydrogen evolution during the negative-going scan. In this Cd system, only Cd UPD was deposited in the potential range (+0.20 to –0.85 V) because the Cd coverages from charges were
Figure 3.2 Cyclic voltammogram and corresponding $\Delta f$ on a Au-coated AT-cut quartz crystal in a solution containing 0.5 mM CdSO$_4$ and 50 mM Na$_2$SO$_4$, pH = 5.0. The scan rate was 5.0 mV s$^{-1}$. 
less than one full ML. No evidence of bulk Cd was observed although the formal potential for 
\( \text{Cd}^{2+}/\text{Cd}^0 \) was \(-0.697 \text{ V vs. Ag|AgCl|3 M NaCl}\).

Electrodeposition of Se on Au and Ag electrodes has been previously reported [62-64].

Figure 3.3 shows a cyclic voltammograms and corresponding \( \Delta f \) for a Au-coated quartz crystal in contact with the Se solution. When the potential was scanned negatively from +0.27 to +0.070 V, the small reductive peak corresponds to Se UPD (0.060 ML). However, the \( \Delta f \) result (7.9 Hz) indicated loss of mass from the electrode. This is likely to correspond to desorption of Se-containing species (possibly HSeO\(_3\)\(^-\) ions) that may form a network-like structure on the Au electrode. When adsorbed HSeO\(_3\)\(^-\) ion next to the Au electrode was reduced to Se, the structure of adsorbed HSeO\(_3\)\(^-\) ion was no longer stable, resulting in desorption of the adsorbed HSeO\(_3\)\(^-\) and the mass loss. When the potential was scanned further from +0.070 to –0.50 V, and reversed for a positive-going scan to –0.32 V, the reductive current was assigned to Se UPD (0.74 ML), accompanied with a large \( \Delta f \). Plots of the measured charges vs. corresponding \( \Delta f \) yielded M/z values (40.0 and 21.0 g equivalent\(^{-1}\)), compared to the theoretical value (19.7 g equivalent\(^{-1}\)) for Se deposition via a four-electron process. The results suggest that initially Se deposition is accompanied by adsorption of a species in the Se solution. At more negative potential, Se continues to deposit while the adsorbed ion remains on Se UPD. In the potential range of \(-0.20\) to +0.46 V, the charging current was accompanied with the positive change (7.8 Hz) in \( \Delta f \) values. This is assigned to desorption of ion adsorbed on Se UPD in the negative-going scan. When the potential was in the range of +0.46 and +1.02 V, two oxidative peaks corresponded to stripping of Se UPD. The \( \Delta f \) values increased in the potential range of +0.46 to +0.72 V, corresponding to oxidation of Se UPD. From the potential range of +0.72 to +1.02 V, no
Figure 3.3  Cyclic voltammogram and corresponding Δf on a Au-coated AT-cut quartz crystal in a solution containing 0.5 mM SeO₂ and 50 mM Na₂SO₄, pH = 5.0. The scan rate was 5.0 mV s⁻¹.
significant change in $\Delta f$ values was observed because the stripping of Se UPD and re-adsorption of HSeO$_3^-$ ion occurred at the same time. When the potential was scanned further, the current and $\Delta f$ were assigned to oxidation of Au, rather than oxidation of Se. This is confirmed by the presence of the cathodic peak, centered at +0.68 V, and the positive change in $\Delta f$ values. The Se coverage (0.72 ML) calculated from the oxidative charges was very close to that (0.80 ML) calculated from the reductive charges. The result suggests that Se UPD was deposited in the potential range used in this study via a four-electron process, and no evidence of six-electron reaction was observed.

The flow cell EQCM was used to form CdSe with various deposition programs. Before a deposition was started, the Au-coated quartz crystal was electrochemically cleaned according to the cleaning procedure described in the experimental section. To form CdSe, an EC-ALE cycle consisted of a sequence of steps to deposit constituent elements (Cd and Se) at UPD potentials. Solutions, containing Cd$^{2+}$ and Se$^{4+}$ ions, were alternately rinsed through the deposition cell for 20 s. The blank solution was used to flush the deposition cell for 100 s to prevent mixing of ions, leading to co-deposition. Solutions were continuously flowed to the deposition cell at constant rate of 0.45 mL min$^{-1}$, using pressurized container. The cycle was repeated as needed to form CdSe with a desired thickness.

In this part, the objective was to study the effect of potential shifts to the growth of CdSe. Six series of CdSe deposition were carried out with linear potential steps (0, –10, –30, –40, –50, and –70 mV) from the 3$^{rd}$ through 6$^{th}$ cycles. In the first two cycles, the deposition programs were designed to form two monolayers of CdSe. This was to modify the bare Au electrode to CdSe-covered Au electrode, allowing studies of deposition of Cd and Se without the influence of the Au electrode. Figure 3.4 shows current and $\Delta f$ traces for six cycles of CdSe with potential
Figure 3.4 Current and $\Delta f$ traces for CdSe deposition using EC-ALE on a Au-coated quartz crystal when the applied potential was negatively stepped after the second cycle for (a) 0.0, (b) –50, and (c) –70 mV. The potential for the 1$^{st}$ Se step was –0.10 V. The deposition potential was stepped from –0.10 to –0.30 V at the 1$^{st}$ Cd step and remained at the potential until the end of the 2$^{nd}$ cycle.
Deposition Time/ks

I/µA

Δf/kHz

(b)
step of (a) 0.0, (b) –50, and (c) –70 mV after the 2nd cycle. Se was deposited first, followed by Cd. In Figure 3.4(a), the reductive current and $\Delta f$ steadily decreased from the 3rd through 6th cycles, indicating that smaller amounts of Cd and Se were deposited at the potential of –0.30 V. It has been reported earlier that UPD potential of Cd on the Au electrode is more positive than that on the Se-covered Au electrode [65]. Thus, it is obvious that potential step is required to continue to grow a thicker CdSe using EC-ALE. In Figure 3.4(c), when the potentials were linearly stepped after the 2nd cycle, the charges passed and $\Delta f$ for both Cd and Se increased simultaneously. The coverages of Cd and Se calculated from the measured data increased from 0.40 to 1.00 ML during the 3rd through 6th cycles. The model of zinc blende CdTe on Au(111) was previously reported, suggesting that one ML of CdTe required 0.44 ML of Cd and Te vs. the number of surface atoms of Au(111) electrode [66]. It is thus assumed here that one full ML of CdSe consists of two atomic layers of Cd and Se with coverage of 0.44 ML. The results from Figure 3.4(c) indicated that the potential shift (–70 mV per cycle) was too large, and excess Cd and Se were deposited. In Figure 3.4(b), from the 3rd through 6th cycles, the values of charges passed and $\Delta f$ for Cd and Se steps were similar, and the calculated coverages of Cd and Se from charges and $\Delta f$ were shown in Figure 3.5. The Se coverages calculated from coulometry and $\Delta f$ were ~0.6 ML, close to the expected value, 0.44 ML. In case of Cd, the coverages (~0.4 ML) calculated from charges were higher than that (~0.2 ML) calculated from $\Delta f$. The extra charge corresponded to oxygen reduction. It is demonstrated here that the potential step of –50 mV could be used to deposit atomic layers of Cd and Se without resulting in bulk deposition. In addition, the results confirm that it is necessary to shift potentials to more negative values as the number of deposition cycles increases to continue to grow films of compound semiconductors using EC-ALE.
Figure 3.5 Calculated coverages for CdSe deposition as a function of deposition cycles with the potential step of –50 mV after the 2nd cycle: (○) Cd, charge; (●) Cd, Δf; (□) Se, charge; (■) Se, Δf.
In this section, attempts were made to optimize deposition programs for CdSe from a bare Au electrode. A series of CdSe deposition was carried out, using the flow cell EQCM. Various deposition programs were written where the starting potential was set at –0.30 V for both Cd and Se steps. The final potentials, generally more negative than the starting potential, were varied. A logarithmic function was used to shift deposition potential from the starting to final potentials over a certain number of deposition cycles, such as 10, 20, or 30 cycles. During deposition, the charges and $\Delta f$ were measured. The total measured $\Delta f$ values at the end of deposition were used to roughly evaluate various deposition programs used to form CdSe via EC-ALE. Table 3.1 shows the total $\Delta f$ values for 40 cycles of CdSe with three different deposition programs. From the program A, the total $\Delta f$ value of –690.0 Hz was much smaller than the expected $\Delta f$ (–1778.0 Hz) for 40 cycles of CdSe. This indicated that the deposition potentials were not negative enough to deposit atomic layers of Cd and Se to form CdSe in each cycle. From the program B, the final potentials for both Cd and Se steps were –0.65 V. Although the potential is very close to the formal potential of Cd$^{2+}$/Cd$^0$ system, no bulk Cd was observed during the deposition. With the program B, the total $\Delta f$ value was –1257.0 Hz, less than the expected value by –521.0 Hz. The result suggested that the potential of –0.65 V can be used as steady state potential to deposit CdSe. However, the potential shifts in the first 30 cycles were not enough to deposit 0.44 ML of Cd and Se to form CdSe. The solution was to shift the deposition potentials over 10 cycles instead of 30 cycles, resulting in larger potential changes in the first 10 cycles (Figure 3.6). From the program C, the total $\Delta f$ value (–1727.0 Hz) was very close to the theoretical value (–1778.0 Hz), indicating the formation of a stoichiometric CdSe. The result suggested that the program C was suitable to be used to deposit CdSe via EC-ALE.
Table 3.1 The total $\Delta f$ for 40 cycles of CdSe grown on the Au-coated quartz crystal. The starting potential was $-0.30$ V.

<table>
<thead>
<tr>
<th>Program</th>
<th>Cd potential/V</th>
<th>Se potential/V</th>
<th>Stepping cycles</th>
<th>$\Delta f$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$-0.55$</td>
<td>$-0.58$</td>
<td>30</td>
<td>$-690.0$</td>
</tr>
<tr>
<td>B</td>
<td>$-0.65$</td>
<td>$-0.65$</td>
<td>30</td>
<td>$-1257.0$</td>
</tr>
<tr>
<td>C</td>
<td>$-0.65$</td>
<td>$-0.65$</td>
<td>10</td>
<td>$-1727.0$</td>
</tr>
</tbody>
</table>
Figure 3.6 Plots of potential sets used for the deposition of CdSe (40 cycles) via EC-ALE method. The starting and final potential were –0.30 and –0.65 V, respectively. The deposition potentials were shifted logarithmically over 10 (▲) and 30 (●) cycles.
Deposition Cycle

E/V vs. Ag|AgCl|3 M NaCl
Figure 3.7 shows the calculated coverages for CdSe deposition from charges passed and Δf as a function of deposition cycles. The coverages were reported vs. one full ML of zinc blende CdSe formed on Au(111). From coulometry, the Cd coverages in the 1st and 2nd cycles were 0.71 and 1.40 ML, respectively, while for Se the coverages were 0.91 and 1.05 ML. In the 1st cycle, a monolayer of Cd partially covered the Au electrode. The deposited Cd may form a loosed structure or large islands with one atomic height. When Se was deposited, a ML of Se was formed on both Cd UPD and Au electrode. In the 2nd cycle, more than one ML of Cd was deposited, followed by one ML of Se. It has been shown in this group that when Cd was deposited on Te-covered Au electrode, the place exchange between Cd and Te occurred, due to the higher infinity of Cd and Au [66]. The reason is that Cd prefers to bond to Au atoms, and half of the deposited Cd penetrates through Te layer to bond directly to Au. It was assumed that this also happens in CdSe system. The diffusion of Cd through Se layers was confirmed by the results from Δf. In the 1st and 2nd cycles, the coverages (0.45 and 1.37 ML) were added together and agreed well with the formation of 2 full ML of CdSe. From the 3rd through 25th cycles, the coverages calculated from charges were much higher than that calculated from Δf. The extra charge corresponds to oxygen reduction. In case of Δf, the coverages decreased down to ~0.7 ML for six cycles and started to increase again to 1.07 ML. After the 25th cycle, the coverages of Cd and Se from coulometry and Δf were close to one another in the range of 0.95-1.15 ML. The results indicate that the deposition program is optimized for the formation of CdSe using EC-ALE. Additional studies have been initiated to improve the deposition condition in the first 10 cycles.
Figure 3.7  Calculated coverages for CdSe deposition as a function of deposition cycles: (■) Cd, charge; (▲) Se, charge; and (●) CdSe, Δf.
Conclusions

A flow cell EQCM was used to study the electrodeposition of Cd and Se in acidic solution. In the potential range, Cd UPD was deposited without any evidence of bulk deposition. The adsorption of SO$_4^{2-}$ ion was observed on Cd UPD as evident from the large mass change. The electrodeposition of Se occurred under a four-electron process. No evidence of a six-electron process, producing H$_2$Se, was observed. From the M/z values, Se UPD was accompanied with adsorbed species. The effect of potential shifts for CdSe deposition was carried out on CdSe-covered Au electrode. Potential shift of −50 mV was required to deposit atomic layers of Cd and Se as the number of deposition cycles increased because the UPD potentials of Cd and Se were more negative than those on a bare Au electrode. The flow cell EQCM was also used to grow 40 cycles of CdSe from a bare Au electrode with various deposition programs. It was found that the optimized deposition condition for the formation of CdSe using EC-ALE was to use −0.30 and −0.65 V as the starting and final potentials, respectively, with 10-stepping cycle.

References


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CHAPTER 4

FLOW CELL ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE (EQCM)

STUDIES OF THE FORMATION OF PBTE VIA EC-ALE\(^1\)

\(^1\)Srisook, N. and J.L. Stickney. To be submitted to *Electrochimica Acta.*
Abstract

A flow cell electrochemical quartz crystal microbalance (EQCM) was used to study the deposition of PbTe via electrochemical atomic layer epitaxy (EC-ALE). It is a deposition method based on atomic layer epitaxy (ALE), where a deposit is grown in a layer-by-layer fashion, promoting two-dimensional growth. Electrochemical surface-limited reactions, underpotential deposition (UPD), are used to deposit layers of constituent elements, forming a compound using EC-ALE. Alternating layers of Pb and Te were deposited on the electrode using UPD potentials, in a cycle. Cyclic voltammetry was used to determine the initial UPD and bulk potentials for both Pb and Te. Three series of PbTe depositions were carried out by varying deposition potentials for Pb and Te. All other deposition conditions were kept constant during a series. The solution flow rate of 6.1 mL min\(^{-1}\) was used. Current and \(\Delta f\) were simultaneously recorded as a function of time and the number of cycles. Coverages were calculated based on the formation of a monolayer of PbTe. Optimized deposition potentials for Pb and Te were determined as \(-0.47\) and \(-0.60\) V, respectively.

Introduction

IV-VI compound semiconductors have narrow energy bandgap and crystallize in the cubic rock salt structure. Due to their optical properties, the compounds are practical materials for the fabrication of several infrared optoelectronic devices, such as lasers, detectors, light-emitting diodes (LEDs), and photodiode arrays [1, 2]. Pb chalcogenides have large Bohr radius and are excellent materials for studies of quantum confinement effects [3]. In addition, PbTe can be used in thermoelectric applications, such as coolers or power generators [4-6].

There are three epitaxial deposition techniques that have been conventionally used to grow IV-VI compound semiconductors: liquid phase epitaxy (LPE) [7], hot wall epitaxy (HWE)
Among these techniques, MBE is the best method because it produces electronic-grade deposits with accurate control over composition, doping, and structure. Elemental precursors are thermally evaporated, and beams of atomic or molecular precursors impinge on a crystalline substrate, held at high temperature. Depositions are carried out in an ultra high vacuum chamber, and the precursors travel line of sight, collision-free, to the substrate. These reactants impinge on the surface, forming a solid deposit. The film growth is generally controlled by temperature and the flux of precursors arriving at the substrate. The growth rate is about one atomic layer per second. When hetero or multilayer structures are formed, interlayer diffusion of elements often occurs, resulting in blurred interface between layers. In addition, since films are formed above room temperature, defects can form as the deposit cools, the result of differential thermal expansion coefficients. Another drawback of MBE is the high cost.

Electrodeposition is a low-cost deposition method compared to MBE. Deposition occurs in a solution phase, generally at ambient temperature and pressure. No sophisticated hardware is necessary, and maintenance requirement is low. Precursors are dilute solutions of inorganic salts, generally less toxic than the gaseous precursors used in MBE or chemical vapor deposition (CVD) [16-18]. Deposit can also be uniformly grown on irregular-shaped substrates.

Co-deposition, where all precursor ions are contained in a single deposition bath, has been the primary compound electrodeposition methodology for semiconductors [19]. Co-deposition is carried out by applying a constant potential or current density. Although co-deposition is a very simple methodology, it is often difficult to control both composition and structure in growing films. For example, co-deposited ZnSe films were non-stoichiometric, with
extra Se [20, 21]. Post-deposition treatments, such as annealing at high temperature under inert atmosphere, were generally used, allowing diffusion of extra Se out of the films.

Electrochemical atomic layer epitaxy (EC-ALE) is a deposition method that has been used to form a wide variety of compound semiconductors [22-25]. It is the electrochemical analog of atomic layer epitaxy (ALE), where deposits are grown layer-by-layer [26-28]. In ALE, surface-limited reactions are used. In EC-ALE, the surface-limited reactions are called underpotential deposition (UPD), and are used to deposit the constituent elements forming a compound one atomic layer at a time. UPD is a well-known electrochemical reaction where one element is deposited on a second at potentials prior to that required for the first to deposit on itself [29-31]. The driving force is the free energy change from bonding between the two elements. In EC-ALE, a cycle consists of a sequence of steps for depositing atomic layers of constituent elements to form a compound. In each step, deposition conditions (potential, time, precursors, and pH) can be independently optimized, allowing EC-ALE more flexible than co-deposition. In addition, films grown using EC-ALE promotes layer-by-layer growth, avoiding three-dimensional growth, providing more control of film composition and morphology.

A significant number of compound semiconductors have been grown using the EC-ALE method, including the cadmium chalcogenides [32-37], CdZnS and CdZnSe [38], ZnSe [39], In$_2$Se$_3$ [40], PbS [41], PbSe [42], and Bi$_2$S$_3$ [43]. The compositions of deposits have been initially investigated by measuring charges during deposition steps. Faraday’s law is used to calculate the coverage of element being deposited, and the number of electrons transferred is assumed to be equivalent to the oxidation state of the depositing element in its precursor ion. For example, when Pb$^{2+}$ and HTeO$_2^+$ ions are used as precursors, the number of electron being transferred for Pb and Te are two and four, respectively. When PbTe is deposited via EC-ALE,
charges passed during the Pb deposition step should be half that for the Te step. However, some side reactions can occur simultaneously with the deposition, obscuring the deposition charge. For example, if the deposition is carried out at potentials where hydrogen evolution occurs, coverages will be over estimated. In addition, trace oxygen in the deposition solution can be reduced, especially in the presence of Pb UPD [44]. Both reactions result in excess reduction charge, resulting in errors in the analysis of film composition.

To better understand the formation of compound semiconductors via EC-ALE, a flow cell electrochemical quartz crystal microbalance (EQCM) has been constructed and used to measure mass changes during the depositions [45]. A EQCM is a mass-sensing device that is capable of measuring small mass changes on its surface [46-48]. In this case, a 9-MHz QCM was used, with a mass sensitivity less than 2.5 nmol cm\(^{-2}\). When mass is added onto a QCM electrode, a frequency change (\(\Delta f\)) in the quartz crystal is measured. The relationship between \(\Delta f\) and the mass change (\(\Delta m\)) is linear and described by the Sauerbrey equation [49], shown below.

\[
\Delta f = \frac{2nf_o^2}{\sqrt{\mu \rho}} \Delta m = -C_f \Delta m
\]

where \(\Delta f\) is the measured frequency change (Hz), \(f_o\) is the resonance frequency of the quartz crystal, \(\Delta m\) is the change in mass per unit area (g cm\(^{-2}\)), \(\rho\) (2.648 g cm\(^{-3}\)) is the density of quartz, \(\mu\) (2.947 x 10\(^{11}\) g cm\(^{-1}\) s\(^{-2}\)) is the shear modulus of quartz, \(n\) is the number of the harmonic at which the crystal is driven, and \(C_f\) (Hz cm\(^2\) g\(^{-1}\)) is the sensitivity factor [46]. The negative sign in the Sauerbrey equation indicates that \(\Delta f\) decreases when mass is added to the QCM electrode and
vice versa. EQCM has been used to study the electrodeposition of several compound semiconductors, such as CdSe [50], CdTe [51, 52], PbS [53], PbSe [54, 55], and PbTe [56].

In this paper, the flow cell EQCM was used to study the formation of 10-cycle deposits of PbTe via EC-ALE. The deposition was performed under continuous solution flow of 6.1 mL min\(^{-1}\). In the PbTe deposition cycle, Te was deposited first, followed by Pb. The potentials used to deposit Pb and Te were selected initially based on cyclic voltammograms of the elements. Three deposits of PbTe were performed, in which the potentials for Pb and Te were adjusted. Both currents and \(\Delta f\) were recorded simultaneously as a function of time. Coverages were calculated with respect to a full ML of zinc blende PbTe(111). From these results, optimized deposition potential for PbTe were suggested.

**Experimental**

The automated electrochemical deposition system, used to study the deposition of PbTe, has been previously described [45], consisting of a flow cell EQCM, a series of solution reservoirs, a distribution valve, a potentiostat, an oscillator unit, and a frequency counter. A variable speed peristaltic pump (Cole-Parmer, Vernon Hills, IL) was used to pump solutions. The deposition system was controlled via a Pentium-based computer equipped with a PCLD-812PG interface board (Advantech, Irvine, CA). The deposition programs were written in LabView 4.0 (National Instruments, Austin, TX). The flow cell EQCM consisted of a Au-coated quartz crystal, sandwiched between two Plexiglas blocks with two Silicone gaskets. Machine bolts were used to hold the cell together. The auxiliary electrode was a thin Au wire, and the reference electrode was Ag/AgCl|3 M NaCl (Bioanalytical Systems, Inc., West Lafayette, IN). The flow cell EQCM, connected to an oscillator unit (Seiko EG&G, Model: QCA917-11), was housed in a Plexiglas box, and a home-made Faraday cage was used to eliminate electrical
interference in $\Delta f$ measurements. A second Plexiglas box was used to house all solution containers. Nitrogen gas was used to purge the Plexiglas boxes, dropping the oxygen partial pressure.

AT-cut quartz crystals were purchased from Seiko EG&G. The crystals were coated on both sides with evaporated Au layer (300 nm) on Ti adhesion layers (50 nm). Before use, the quartz crystals were cleaned in conc. H$_2$SO$_4$ for 5 mins in an ultrasonic cleaner (Cole-Parmer, Vernon Hills, IL). They were then rinsed thoroughly with de-ionized water and carefully blown dry with nitrogen gas. The crystals were finally assembled into the flow cell, described above.

All reagents were analytical grade or better. The Pb(ClO$_4$)$_2$ (Aldrich) concentration was 0.2 mM, pH 5.5, with 50 mM CH$_3$COONa.3H$_2$O (J.T.Baker). The TeO$_2$ (Aldrich) concentration was 0.2 mM, pH 9.2, buffered with 50 mM Na$_2$B$_4$O$_7$.10H$_2$O (J.T.Baker). A blank solution, prepared from 0.1 M NaClO$_4$ (Alfa Aesar), pH 5.5, was used to rinse electroactive ions out of the deposition cell, preventing co-deposition. Solution pHs were adjusted with HClO$_4$ (J.T.Baker). The supporting electrolyte for all deposition solutions was 0.1 M NaClO$_4$. A 10 mM HClO$_4$ solution was used to clean the electrode before and after depositions. De-ionized water (18.0 MΩ cm), obtained from a NANOpure UV ultrapure water system (Barnstead International, Dubuque, IA), was used to prepare all solutions.

The EQCM electrode was electrochemically cleaned according to the following procedure. The cleaning solution, 10 mM HClO$_4$, was continuously rinsed through the deposition cell at ~0.4 mL min$^{-1}$. Three cycles of potential steps between +1.30 and −0.30 V were used to oxidize and reduce the electrode. Under constant solution flow, all products were rinsed from the deposition volume, avoiding their re-deposition on the electrode. After cleaning, the blank solution was used to rinse the 10 mM HClO$_4$ solution from the cell.
The Au electrode surface area was measured electrochemically using the oxygen adsorption method [57]. The method is based on the belief that a monolayer (ML) of oxygen adsorbs on the Au electrode just prior to oxygen evolution. An elemental monolayer is referenced to the number of surface atoms on the Au substrate, one to one. A cyclic voltammogram of the Au-coated quartz crystal was carried out in 0.1 M HClO₄ in the potential range of –0.30 to +1.42 V. Just positive of +1.42 V, the current increased abruptly, indicating oxygen evolution. The charge passed during the subsequent reduction of the Au oxide was determined, and Faraday’s law was used to calculate the number of oxygen atoms. The number of Au atoms is assumed equal to the number of oxygen atoms. Assuming predominant (111) texture, the Au electrode area was determined to be 0.299 cm² (4.038 x 10¹⁴ atoms).

The EQCM was calibrated by using Ag electrodeposition and cyclic voltammetry. The Ag solution consisted of 2 mM AgNO₃ and 0.1 M HClO₄. A cyclic voltammogram was obtained over the potential range of +0.85 to +0.10 V, under static conditions (no solution flow). The values of Δf were plotted against the integrated current. From the slopes, the average calibration constant was determined as 4.77 ng cm⁻² Hz⁻¹.

Results and Discussion

The electrodeposition of Pb has been previously studied on metal electrodes, such as Pt, Au, and Ag [58-64]. Figure 4.1 shows a cyclic voltammogram and corresponding Δf values for the Au-coated quartz crystal in contact with the Pb solution. In the potential range of –0.020 and –0.53 V, two cathodic peaks are visible, resulting in a Δf (–52.7 Hz), corresponding to Pb UPD. A Pb coverage of 0.72 ML was calculated from the charges, almost twice that calculated from the measured Δf (0.49 ML). The extra charge corresponds to the reduction of oxygen dissolved in the solution. Although the deposition system was purged with nitrogen to eliminate oxygen
Figure 4.1 A cyclic voltammogram and corresponding $\Delta f$ for a Au-coated quartz crystal in a solution containing 0.2 mM Pb(ClO$_4$)$_2$ in 50 mM CH$_3$COONa and 0.1 M NaClO$_4$, pH = 5.5 under static condition. The scan rate was 5.0 mV s$^{-1}$. 
E/V vs. Ag|AgCl|3 M NaCl

I/µA

V

Hz
contamination, an oxygen level of 15 ppm was still present. Despite of the small amount of oxygen, the large current observed was facilitated by Pb UPD catalyzed reduction of oxygen [65, 66]. When the potential was scanned further, the reductive current and Δf increases abruptly as bulk Pb deposition was initiated, and continued as the potential was reversed. The formal potential for Pb$^{2+}$/Pb$^0$ was –0.496 V. The fact that the reductive current was greater in the positive going scan, for bulk deposition, suggests nucleation and growth. When the potential was scanned further positive, the three oxidative peaks, and corresponding Δf features, were assigned to the stripping of bulk Pb and the two Pb UPD processes. The large separation (~0.1 V) between the last two stripping peaks may indicate some degrees of alloying between the initially deposited Pb and the Au electrode. Green and Hanson reported Au(111) electrodes roughened after stripping a monolayer of Pb, suggesting a Pb-Au alloying had formed [67]. In Figure 4.1, there was no mass difference between the starting and ending points. This indicates that all the Pb was stripped, including any Pb involved in alloy formation, by scanning the potential up to +0.40 V.

Te electrodeposition has been reported in the literature [68-72]. The reduction of Te(IV) is complex and can occur by several pathways. Figure 4.2 shows a cyclic voltammogram and corresponding Δf for a Au-coated quartz crystal in contact with the Te solution. When the potential was scanned negatively from +0.20 V, no significant current was measured, but Δf increased significantly, indicating a mass loss rather than deposition. This suggests desorption of a species (ClO$_4^-$, H$_2$O, TeO$_3^{2-}$, etc.). It has been earlier reported that Te-containing species adsorb on Au electrodes, prior to Te deposition in an acidic solution [71, 72]. Given those results, it is believed that the species adsorbed on the Au electrode are TeO$_3^{2-}$ related, and the increase in Δf corresponds to their desorption from the electrode. Their desorption appears to be
Figure 4.2 A cyclic voltammogram and corresponding $\Delta f$ for a Au-coated quartz crystal in a solution containing 0.2 mM TeO$_2$ in 50 mM Na$_2$B$_4$O$_7$ and 0.1 M NaClO$_4$, pH = 9.2 under static condition. The scan rate was 5.0 mV s$^{-1}$. 
related to the initial reductive deposition of Te atoms. In the potential range of $-0.071$ to $-0.65$ V, cathodic currents corresponding to Te UPD (0.43 ML) are accompanied by a significant negative $\Delta f$. From graphs of M/z over this potential range, it is evident that initially, ($-0.25$ to $-0.45$ V) the M/z value is 58.0 g equivalent$^{-1}$, rather than the 31.9 g equivalent$^{-1}$ expected for Te. This suggests that there is some adsorption commensurate, possibly a telluryl species. When the potential was scanned further, to $-0.80$ V, and reversed back to $-0.60$ V, $\Delta f$ and coulometry agreed, suggesting bulk Te deposition. Measured values of $\Delta f$ were plotted against charge, resulting in a linear graph, with a slope, M/z, 32.2 g equivalent$^{-1}$, very close to the theoretical value (31.9 g equivalent$^{-1}$) for Te deposition through a four-electron process. In the potential range of $-0.60$ to 0.0 V, the minimal current was accompanied by a net positive $\Delta f$ (~7.0 Hz). This mass loss may result from desorption of adsorbed species, possibly HTeO$_2^+$, on the Te-covered electrode. Such a mass loss would be consistent with loss of an adsorbed species, such as that felt to have adsorbed during Te UPD, discussed above when the excessive M/z values were observed. The origin of the mass loss requires additional studies. In the potential range of $-0.10$ and $+0.20$ V, oxidation takes place along with a dramatic increase in $\Delta f$, corresponding to bulk Te stripping. Positive of $+0.20$ V, $\Delta f$ drops as Te UPD is stripped from the surface, and the TeO$_3^{2-}$ species is re-adsorbed, leading to a net increase in mass.

With EC-ALE, deposition is performed in a cycle, consisting of the alternated deposition of atomic layers of the constituent elements to form a compound. Each element is deposited with potential control, using UPD, to form the atomic layers. Figure 4.3 is a diagram of the deposition programs used to form 10 cycles of PbTe. The first three cycles were drawn to show the order for the solutions, the timing, and the deposition potentials. The solution flow rate was 6.1 mL min$^{-1}$. Although higher flow rates could be used, the noise level in $\Delta f$ measurements
Figure 4.3  A diagram for PbTe deposition program showing solution orders, deposition times, and applied potentials.
would increase, resulting in larger coverage errors. Before deposition, the EQCM electrode was cleaned according to the procedure described in the experimental section. To initiate the deposition program, blank solution was pumped through the deposition cell for 100 sec to stabilize the frequency of quartz crystal. Te solution was then rinsed through for 30 sec for Te deposition. Blank was pumped in for five sec to rinse out TeO$_3$$^{2-}$ ions, at the same potential used to deposit Te. Pb solution was then rinsed through for 30 sec for Pb deposited, on top of the Te atomic layer. The deposition cell was then rinsed again with blank for 5 sec. The total deposition time for one cycle was 70 s, one cycle of PbTe deposition via EC-ALE. The cycle was then repeated 10 times to finish the PbTe deposition.

In this section, the objective was to optimize potentials for PbTe deposition. The UPD potentials for Pb and Te were initially selected by inspection of the cyclic voltammograms discussed earlier. The total $\Delta f$ at the end was used to characterize the amount of PbTe deposited on the Au electrode, to evaluate the resulting deposits. The expected $\Delta f$ was $-777.0$ Hz, corresponding to 10 ML of PbTe. Tables 4.1 and 4.2 show the $\Delta f$ results for the first two sets of PbTe studies. In the first set (Table 4.1), the Pb potential was held at $-0.32$ V, while 10 cycle deposits of PbTe were performed using Te potentials of $-0.20$, $-0.32$, $-0.48$, $-0.60$, and $-0.70$ V. Te potentials positive of $-0.60$ V, resulted in $\Delta f \leq -262.0$ Hz, indicating there was not enough Te to form a full ML of PbTe each cycle. For Te potential of $-0.70$ V, the total $\Delta f$ ($-1658.0$ Hz) suggests that some bulk Te was deposited. The total $\Delta f$ was very close to the expected value when a Te potential of $-0.60$ V was used, suggesting the Te potential was about right. In the second set of studies (Table 4.2), the depositions were performed using a Te potential of $-0.60$ V, while the Pb potential was varied: 0.0, $-0.32$, $-0.47$, and $-0.60$ V. For a Pb potential of 0.0 V, the $\Delta f$ ($-358.8$ Hz) was about half of the expected value. Using a Pb potential of $-0.60$ V
Table 4.1. The total measured $\Delta f$ for 10 cycles of PbTe when the Pb potential was –0.32 V, and the Te potentials were in the range of –0.20 to –0.70 V.

<table>
<thead>
<tr>
<th>Pb Potential/V</th>
<th>Te Potential/V</th>
<th>$\Delta f$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>–0.32</td>
<td>–0.20</td>
<td>–165.0</td>
</tr>
<tr>
<td>–0.32</td>
<td>–0.32</td>
<td>–191.0</td>
</tr>
<tr>
<td>–0.32</td>
<td>–0.48</td>
<td>–262.0</td>
</tr>
<tr>
<td>–0.32</td>
<td>–0.60</td>
<td>–708.0</td>
</tr>
<tr>
<td>–0.32</td>
<td>–0.70</td>
<td>–1658.0</td>
</tr>
</tbody>
</table>
Table 4.2. The total measured $\Delta f$ for 10 cycles of PbTe when the Te potential was –0.60 V, and the Pb potentials were in the range of 0.0 to –0.60 V.

<table>
<thead>
<tr>
<th>Pb Potential/V</th>
<th>Te Potential/V</th>
<th>$\Delta f$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>–0.60</td>
<td>–358.8</td>
</tr>
<tr>
<td>–0.32</td>
<td>–0.60</td>
<td>–708.0</td>
</tr>
<tr>
<td>–0.47</td>
<td>–0.60</td>
<td>–747.9</td>
</tr>
<tr>
<td>–0.60</td>
<td>–0.60</td>
<td>–2890.9</td>
</tr>
</tbody>
</table>
resulted in extensive deposition, $\Delta f$ of $-2890.9$ Hz, suggesting that bulk Pb was deposited. Using a Pb potential of $-0.47$ V, the total $\Delta f$ was essentially equal to the expected value. A Pb potential of $-0.47$ V is very close to the formal bulk potential for $\text{Pb}^{2+/\text{Pb}^0}$ ($-0.496$ V), measured on Au (Figure 4.1). Osipovich et al. reported that Pb UPD on a Te-covered Au electrode occurred at more negative potentials than on bare, clean Au [73]. This indicates that Pb UPD is more stable on Au than on Te-covered Au, so a potential of $-0.47$ V appears reasonable. To confirm that the conditions were optimized, a series of depositions were carried out using a Pb potential of $-0.47$ V and Te potentials of $-0.32$, $-0.47$, $-0.55$, $-0.60$, $-0.65$, and $-0.70$ V. The resulting $\Delta f$ values are shown in Table 4.3. When the potentials were positive of $-0.60$ V, the deposited Te was not enough to form a full ML of PbTe. When the potentials were negative of $-0.60$ V, bulk Te was deposited. The results in Table 4.3 confirm the optimized deposition potentials for PbTe to be $-0.47$ and $-0.60$ V for Pb and Te, respectively.

Figure 4.4 displays current and $\Delta f$ as a function of times for the deposition of 10 cycle of PbTe using $-0.47$ and $-0.60$ V for Pb and Te, respectively. All solutions were pumped through the cell at the constant flow rate of 6.1 mL min$^{-1}$. A blank solution was rinsed though the deposition cell at $-0.60$ V, and the background current ($\sim 1$ µA) corresponded to the reduction of trace amount of oxygen. The deposit was initiated with a Te deposition step, and displays a significant Te reductive current, accompanying a large negative $\Delta f$. The Te coverage (4.1 ML) calculated from $\Delta f$ was much larger than the 0.61 ML calculated from the charge passed. The extra mass probably corresponds to the adsorption of a tellurite species, $\text{TeO}_3^{2-}$, contained in the Te solution. Varazo et al. recently reported that Te-containing species were present after Te deposition on a Cd-covered Au electrode [74]. Thus, it is assumed here that in addition to deposited Te, an adsorbed species such as $\text{TeO}_3^{2-}$ ions were present. When the blank was rinsed
Table 4.3. The total measured $\Delta f$ for 10 cycles of PbTe when the Pb potential was –0.47 V and the Te potentials were in the range of –0.32 to –0.70 V.

<table>
<thead>
<tr>
<th>Pb Potential/V</th>
<th>Te Potential/V</th>
<th>$\Delta f$/Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>–0.47</td>
<td>–0.32</td>
<td>–177.4</td>
</tr>
<tr>
<td>–0.47</td>
<td>–0.47</td>
<td>–264.5</td>
</tr>
<tr>
<td>–0.47</td>
<td>–0.55</td>
<td>–381.5</td>
</tr>
<tr>
<td>–0.47</td>
<td>–0.60</td>
<td>–747.9</td>
</tr>
<tr>
<td>–0.47</td>
<td>–0.65</td>
<td>–1089.2</td>
</tr>
<tr>
<td>–0.47</td>
<td>–0.70</td>
<td>–2505.1</td>
</tr>
</tbody>
</table>
Figure 4.4  Current and Δf traces as a function of deposition time for 10 cycles of PbTe using EC-ALE. The applied potential for Pb and Te were –0.47 V and –0.60 V, respectively. The solution flow rate was 6.1 mL min⁻¹.
through the cell, removing the Te solution, the mass decreased dramatically, suggesting the TeO$_3^{2-}$ species was adsorbed reversibly, and without tellurite in solution, the adsorbed species was unstable and desorbed. When Pb solution was rinsed through the cell, the reductive current was accompanied by a $\Delta f$ of $-45.7$ Hz. The Pb coverage (0.99 ML) calculated from the charges was larger than that (0.41 ML) from the measured $\Delta f$. The extra charge is consistent with a small amount of oxygen reduction, catalyzed by the presence of Pb UPD. The blank was then used to rinse out Pb$^{2+}$ ions from the cell and again there is a significant increase in frequency, suggesting the desorption of adsorbed anions. The deposition cycle was repeated 10 times. Individual coverages for Pb and Te were calculated individually from reductive charges passed. However, it was difficult to calculate individual coverage from the $\Delta f$ data, given the adsorption and desorption of species during the cycle. In an attempt to analyze the data, it was decided to calculate coverage per deposition cycle from the $\Delta f$ results, as described below.

From the data in Figure 4.4, both current and $\Delta f$ were measured as a function of the deposition cycles (Figure 4.5). Coverages were calculated with respect to a full ML of PbTe, consisting of atomic layers of both Pb and Te, rather than with respect to the surface atomic density of Au used for elemental coverages. From previous studies in this group, a model was developed for which a ML of a binary metal chalcogenides was generally considered to be $4/9$th of a ML of each constituent element, with respect to the number of surface atoms in a Au(111) surface [74]. It was thus assumed that one full ML of PbTe consisted of $4/9$ths of a monolayer vs. Au(111), each of Pb and Te.

Figure 4.5 shows the coverages calculated from charges and $\Delta f$ with respect to a full ML of PbTe as a function of the deposition cycle. The straight line was drawn at one ML PbTe, the expected coverage. In the first two cycles, the coverages are higher than expected because the
Figure 4.5  Calculated coverages for PbTe deposition as a function of deposition cycles: (●) Pb, charge; (■) Te, charge; and (▲) PbTe, Δf. The line was drawn at one ML PbTe to show the expected coverage.
deposition potentials are very close to bulk potentials for both Pb and Te, while the amounts of deposits are still influenced by the Au substrate, for which the elements are known to have a high affinity. From the 3rd to 10th cycles, the coverages calculated from charge and ∆f agreed well to one another. The results suggest that one ML of PbTe was formed in each cycle. It is concluded that these potential are suitable to form PbTe monolayers, although the first two cycles are not quite optimized. To obtain a more consistent coverage from cycle to cycle, it is possible to use more positive deposition potentials in the first two cycles, and then use the optimized (steady state) potentials from there on.

Conclusions

Cyclic voltammetry was used to study the electrodeposition of Pb and Te on Au-coated quartz crystal. In the case of Pb deposition, it was found that Pb UPD acted as a catalyst for oxygen reduction, resulting in extra charge. Some evidence of the formation of a Pb-Au alloy was observed. The alloy could be completely stripped, using potentials positive of +0.40 V. The electrodeposition of Te was kinetically controlled, evident by the large separation between reductive and oxidative features. Initial Te deposition occurred simultaneously with desorption of Te-containing species, possibly TeO$_3^{2-}$. The deposition of Te occurred exclusively in a four-electron process as evident by the M/z value of 32.2 g equivalent$^{-1}$. The flow cell EQCM was used to study the formation of PbTe using EC-ALE. A series of PbTe deposition cycles were performed on the Au-coated quartz crystal, using deposition programs where the potentials were varied. From coverage calculations, it was found that the optimized conditions to deposit stoichiometric PbTe were −0.47 and −0.60 V for Pb and Te, respectively.
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CHAPTER 5

CONCLUSIONS AND FUTURE STUDIES
Conclusions

This chapter is intended to summarize the significant results reported in this dissertation. A flow cell electrochemical quartz crystal microbalance (EQCM) has been constructed and used for studies of the electrodeposition of compound semiconductors of metal chalcogenides (CdSe and PbTe) via electrochemical atomic layer epitaxy (EC-ALE). The results can be used to improve deposition programs for the growth of thin films of the compounds.

The construction of the flow cell EQCM has been described in chapter two. The cell design was modified from the flow cells currently used in this group to accommodate the small size of the quartz crystal. The calibration of the EQCM was carried out, using Ag electrodeposition combined with cyclic voltammetry, and the calibration constant value was 5.00 ng cm\(^{-2}\) Hz\(^{-1}\). The noise level of 0.20 Hz in Δf measurements was determined under static conditions (no solution flow). Helium pressure was used to flow solutions to the deposition cell with noise levels comparable to that from the static condition. Alternatively, six-roller peristaltic pump can be used to flow solutions at higher flow rates with acceptable noise level. When solution flow was stopped, shifts in Δf values was observed, corresponding to changes in pressure inside the cell. It was determined that the solution flow rates, equal or less than 70 µL min\(^{-1}\), can be used to avoid the shifts.

The electrodeposition of elements (Cd, Pb, Se, and Te) has been studied, using the flow cell EQCM and cyclic voltammetry. In the potential range of +0.20 to –0.85 V, Cd UPD was deposited on the Au-coated quartz crystal. The extra mass, observed from Δf results, was assigned to co-adsorbed SO\(_4^{2-}\) ion on Cd UPD. In the case of Pb system, Pb UPD was observed in the potential range of –0.020 to –0.53 V. The large separation in the stripping peaks of Pb UPD suggested that Pb-Au alloy occurred during the negative-going scan. For both Se and Te
systems, the electrochemical behaviors were similar. When small amounts of Se and Te were deposited, the mass losses corresponded to desorption of adsorbed ions (HSeO$_3^-$ and TeO$_3^{2-}$). The reductions of Se and Te were found to proceed via a four-electron process. No six-electron reaction, producing H$_2$Se and H$_2$Te, was observed.

The flow cell EQCM has been used for studies of the deposition of CdSe and PbTe via EC-ALE. The UPD potentials were chosen from the cyclic voltammogram of the constituent elements. A series of depositions for the compounds was performed under various potential sets. Both currents and $\Delta f$ were measured as a function of deposition times and used to calculate coverages of depositing elements. The difference in coverages corresponded to reduction of trace oxygen dissolved in solutions. The optimized deposition programs for the depositions of CdSe and PbTe were obtained by comparing the calculated coverages. For CdSe, the optimized deposition programs was to use $-0.30$ and $-0.65$ V as the starting and final potentials with 10-stepping cycle. In the case of PbTe, the stoichiometric deposit was formed, using $-0.47$ and $-0.60$ V as the deposition potentials for Pb and Te, respectively.

**Future Studies**

In the flow cell EQCM, the main issue needed to be solved is the high level of dissolved oxygen in solutions, resulting in extra charges observed during depositions. A degassing method, such as a vacuum degasser, should be used to help reducing the oxygen level. Thus, the interference from oxygen reduction would be at minimum.

The electrodeposition of compound semiconductors (HgSe, HgTe, InSe, and CdTe) via EC-ALE should be studied, using the flow cell EQCM. An optimized deposition condition for the compounds can be obtained. These results can be further used to develop programs for the deposition of HgCdSe, HgCdTe, and CuInSe$_2$. 