ELECTROCHEMICAL QUARTZ CRYSTAL MICROBALANCE (EQCM) STUDIES OF COMPOUND SEMICONDUCTOR AND METAL THIN FILMS FORMATION BY ELECTROCHEMICAL ATOMIC LAYER DEPOSITION (ALD)

By

NAGARAJAN JAYARAJU

(Under the direction of John L. Stickney)

ABSTRACT

Electrochemical atomic layer deposition (ALD) has been developed in this research group to grow thin films of compound semiconductors. It is an electrochemical analog of atomic layer epitaxy (ALE) and atomic layer deposition (ALD), all of which are based on growth of material a monolayer at a time. Under potential deposition (UPD), electrochemical surface limited reactions are used to form the desired materials in a series of steps to form one monolayer at a time. Electrochemical ALD promotes two-dimensional growth, resulting in better control of composition and structure than conventional electrodeposition method. Electrochemical Atomic Layer Deposition (ALD) has recently been used to grow thin films of metals (Cu, Pt on Au) using Surface Limited Redox Replacement (SLRR) reaction. In SLRR, an atomic layer of a less noble metal is replaced by an atomic layer of a more noble metal at Open Circuit.

Electrochemical quartz crystal microbalance (EQCM) is an in-situ mass sensitive device which can measure small changes on its surface. A flow cell EQCM was constructed in our laboratory to study the formation of various compound semiconductors and metal thin films via electrochemical Atomic Layer Deposition (ALD). The regular flow cell was modified to accommodate quartz crystal. Solutions were pushed in to cell either by He pressure or peristaltic pump. Solutions are flowed continiously in to the cell to avoid shifts in Δf values observed when the flow is stopped. Stoichiometry of thin films based on charge and from the electron probe micro analysis (EPMA) doesn't correspond with each other. The extra charges correspond to the side reactions, such as hydrogen evolution, oxygen reduction, and contaminants. EQCM is used to calculate the mass changes during deposition and to better understand the deposition process.

Automated flow cell EQCM was used to grow CdSe, CdTe, HgTe, CdTe/HgTe, Cu and Pt thin films. LabView program is used to run the flow cell. Current and Δf were measured simultaneously as a function of deposition time. The coverage in then calculated based on the charge and mass of deposited elements.

INDEX WORDS: Electrochemistry, Electrodeposition, Thin film, Compound Semiconductor, Electrochemical atomic layer deposition (ALD), Atomic layer epitaxy (ALE), Underpotential deposition (UPD), Electrochemical quartz crystal microbalance (EQCM), Flow cell, CdSe, CdTe, HgTe, CdTe/HgTe, Cu and Pt.

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DEDICATION

To my family: Jayaraju, Jothi, Rajakumari, Kalaiselvi and Mahendiran.

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CHAPTER 1

INTRODUCTION

Materials are grown at the nanoscale in order to have unique and useful properties for semiconductor devices. Atomic layer deposition of compound semiconductors, with two dimensional growth finds applications in electronic and optoelectronic devices, such as transistors, lasers, light-emitting diodes, thermoelectrics and photovoltaics[1-5]. Epitaxial growth of thin films is very important for forming high quality structures and devices for electronic applications. Epitaxy is the growth of a film with a crystallographic relationship the substrate. Films deposited may be homoepitaxial, heteroepitaxial or incommensurate.

The electronic structure, optical properties and band gap can be altered by growing thin films of compound semiconductors, superlattices, nanowires and nanofilms. There are various methods available for the growth of thin films, all based on the growth of a mono or an atomic layer at a time. There are several techniques available for epitaxial growth of compound semiconductors films. Some of the techniques are briefly described in the next two paragraphs.

Chemical vapor deposition (CVD) [6-8] is a deposition method for compound semiconductors (III-V and II-VI groups) used for electronic devices and integrated circuits. Precursor gases (often diluted in carrier gases) are delivered to the reaction chamber at approximately ambient temperatures. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase on the substrate. The substrate temperature is critical and can influence what reactions will take place. A number of CVD techniques, such as Low pressure chemical vapor deposition (LPCVD), Atmospheric pressure chemical vapor deposition (APCVD), metalorganic chemical vapor deposition (MOCVD) are available for different applications. CVD method works at low or atmospheric pressure and at relatively low temperatures.

Molecular beam epitaxy (MBE)[9-13] is one of the most widely used techniques for producing epitaxial layers of metals, insulators and superconductors as well, both at the research and the industrial production level. The principle underlying MBE growth is relatively simple: it consists essentially of atoms or clusters of atoms, which are produced by heating up a solid source. They then migrate in an UHV (10^{-11} Torr) environment and impinge on a hot substrate surface (between 400 and 800^{o}C), where they can diffuse and eventually incorporate into a growing deposit. Precise control on composition, thickness and structure are some of the advantages of MBE. However, ultra high vacuum requirements make the operation very expensive.

The electrochemical method, co-deposition, is commonly used to grow films of compound semiconductors, especially II-VI compounds. Kroger et al. reported CdTe[14] deposition by co-deposition under potentiostatic control. Post-deposition annealing at high temperatures under inert atmosphere is normally used to improve the film properties.

Electrodeposition is generally performed under ambient conditions, avoiding interdiffusion and problems with mismatched thermal expansion coefficients. Electrochemical atomic layer deposition (ALD) has been developed in this research laboratory to prepare thin films of compound semiconductors. It is based on atomic layer epitaxy (ALE)[15-17] and Atomic layer deposition(ALD)[18-21] where deposits are grown layer-by-layer. Surface limited reactions are used, and are generally referred to as underpotential deposition (UPD) for electrochemical systems. An atomic layer of one element can be electrodeposited on a second at a potential under that needed to deposit the element on itself, and this process is referred to as underpotential deposition (UPD). EC-ALE is the use of UPD [22-25] as the surface limited reactions in an ALE cycle. The reaction proceeds as a result of the negative free energy of compound formation, between the element and surface atoms. A monolayer (ML) is defined here as a ratio of adsorbate to electrode surface atoms.

Electrochemical ALD promotes two-dimensional deposit growth and offers better control over composition, structure, and morphology than conventional electrodeposition methods, such as co-deposition. An electrochemical ALD 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. A number of II-VI [26-30], III-V [31, 32], V-VI [33-35] compounds have been successfully deposited by Electrochemical ALD.

An electrochemical quartz crystal microbalance (EQCM) is an in-situ mass sensitive device capable of measuring minute mass changes on its surface, equivalent to the formation of a monolayer while providing conventional electrochemical data at the same time. Piezoelectricity was first pioneered by Raleigh. Thorough investigations were performed by Jacques and Pierre Curie in 1880 and they discovered the piezoelectric effect in various crystals such as quartz, rochelle salt, and tourmaline. Later on, they showed that converse piezoelectric effect also existed. The principle operation of an EQCM is based on the converse piezoelectric effect [36].

A QCM is composed of a thin quartz wafer sandwiched between two metal electrodes, attached to an oscillator circuit. AT-cut quartz crystals are commonly used as QCM due to their low temperature coefficient with only minimal frequency changes. 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 added uniformly added on top of the quartz crystal, the thickness of the quartz crystal changes and a change in the resonance frequency is observed. QCM crystal applications include metal deposition monitors, chemical reaction monitors, biomedical sensors, and environmental monitoring applications and other applications include detection of mass, density, viscosity, adsorption, desorption, and corrosion. The applications of QCM can be found in the Literature [37-40].

QCM have been used in vacuum deposition systems. The 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 [41]. Nomura et al. used the QCM for the electrodeposition of Ag [42]. Bruckenstein et al. also reported the use of QCM to measure mass changes during electrodeposition of Pb and Ag in an acetonitrile solution [43].

The Relationship between the frequency changes to the mass change is given by the Sauerbrey equation:

$$\mathbf{\Delta F = (2nf_0^2 / \sqrt{\mu\rho})\, \Delta m = -C_f \Delta m}$$

ΔF: Measured frequency change (Hz)

Δf_0: Resonance frequency of the quartz crystal (Hz)

Δm: Change in mass per unit area (g cm^{-2})

ρ: Density of quartz ((2.648 g cm^{-3})

μ: Shear modulus of quartz (2.947 x 10^{11} g cm^{-1} s^{-2})

n: Number of the harmonic at which the crystal is driven

C_f: Sensitivity factor (Hz cm^2 g^{-1}).

The negative sign in the Sauerbrey equation indicates that Δf decreases when mass is added to a QCM electrode and vice versa. The relationship between Δf and Δm is linear only when the added mass is less than 2% of the mass of the quartz crystal.

The films grown via Electrochemical ALD, suggested that the films were non-stoichiometric from coulometry. Electron probe microanalysis (EPMA) analysis indicated that the films were stoichiometric. The extra charges may correspond to side reactions, such as hydrogen evolution and oxygen reduction, that can occur during film growth. These reactions would cause the coverages to be overstated when the film composition was calculated from coulometry. EQCM is also used to calculate the mass change when we grow metal thin films, layer by layer by Surface limited redox replacement (SLRR) reactions at open circuit. This work has been done by Adzic and Brankovic [44], Weaver [45] and Dimitrov [46].

A flow cell EQCM was designed as shown in Figure 1.1 and 1.2 and was used in our laboratory to study the deposition of compound semiconductors. Nine MHz AT-cut quartz crystals (Figure 1.3) were purchased from Seiko EG&G. Both sides of the quartz crystal were coated with circular Au electrodes (ca. 0.2 cm^2, 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 N_2. 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 of the Au electrodes, the working electrode was exposed to solution approximately 20 μL, while the other electrode was open to trapped air. A thin Au wire (Wilkinson Company, Inc., Post Falls, ID), placed at the cell outlet, and was used as the auxiliary electrode. All potentials were reported vs. an 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 Δf 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. 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 Δf, 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

Metal electrodeposition (Ag, Cu, and Pb) was used to calibrate the EQCM, assuming 100 % efficiency for the faradaic process. $AgNO_3$ and $HClO_4$ were analytical grade or better. De-ionized water (18.0 M. cm), obtained from a NANOpure UV ultrapure water system (Barnstead International, Dubuque, IA), and was used for all solutions. A plot of Δf vs. Q was linear, and a C_f value was calculated from the slope.

The flow cell EQCM was used to deposit compound semiconductors on a Au-coated quartz crystal to study problems associated with Electrochemical ALD. Current and Frequency change (Δf) were simultaneously measured as a function of the deposition time. The coverages were then calculated based on charge and mass change for the depositing elements. The calculated coverages were compared to better understand the deposition process.

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Figure Captions

Figure 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 no to scale.

Figure 1.2: Diagrams of the flow cell EQCM showing (a) side view and (b) top view.

Figure 1.3: An Au-coated AT-cut quartz crystal, purchased from Seiko EG&G.

Fig 1.1

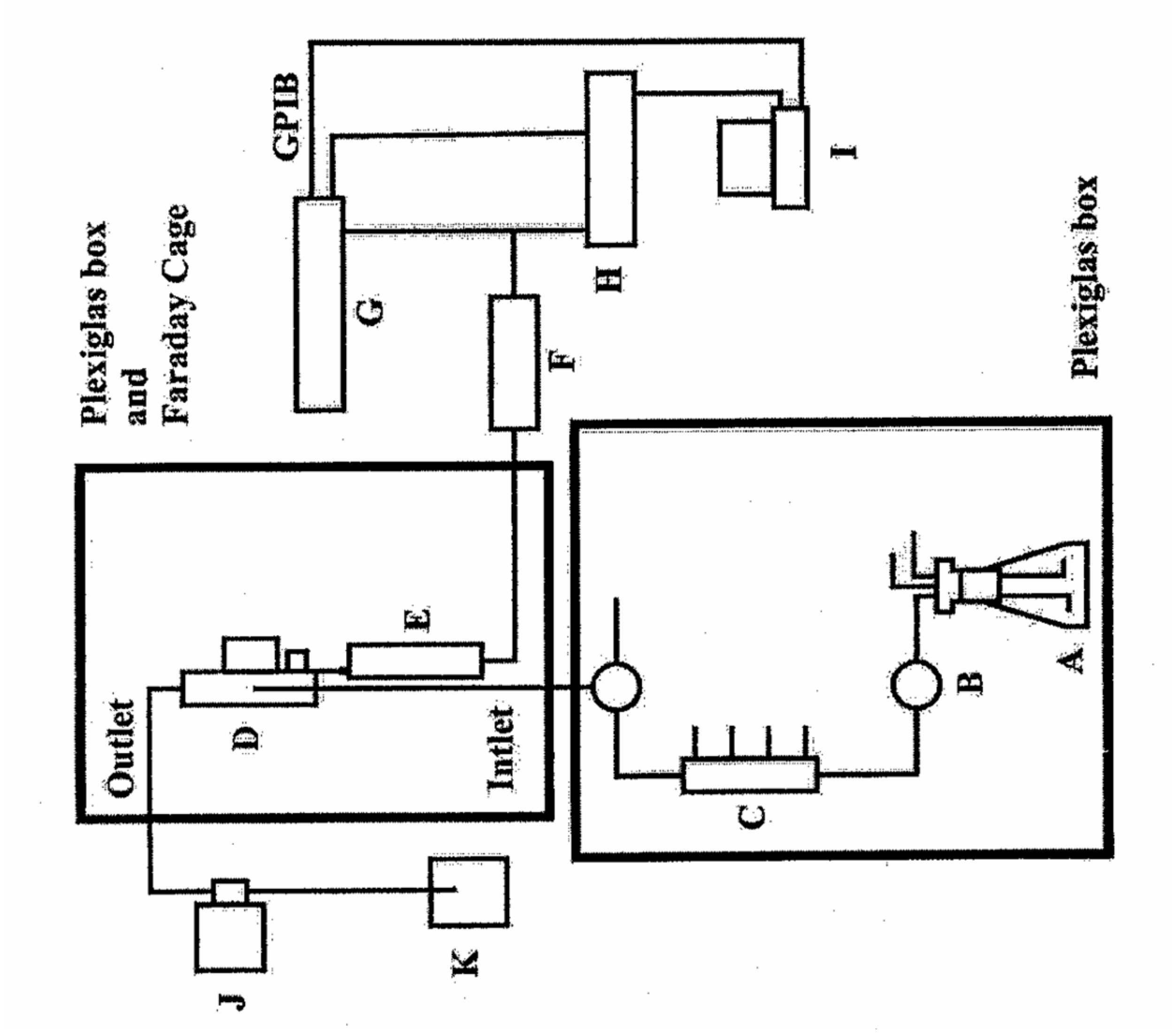
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Fig 1.2

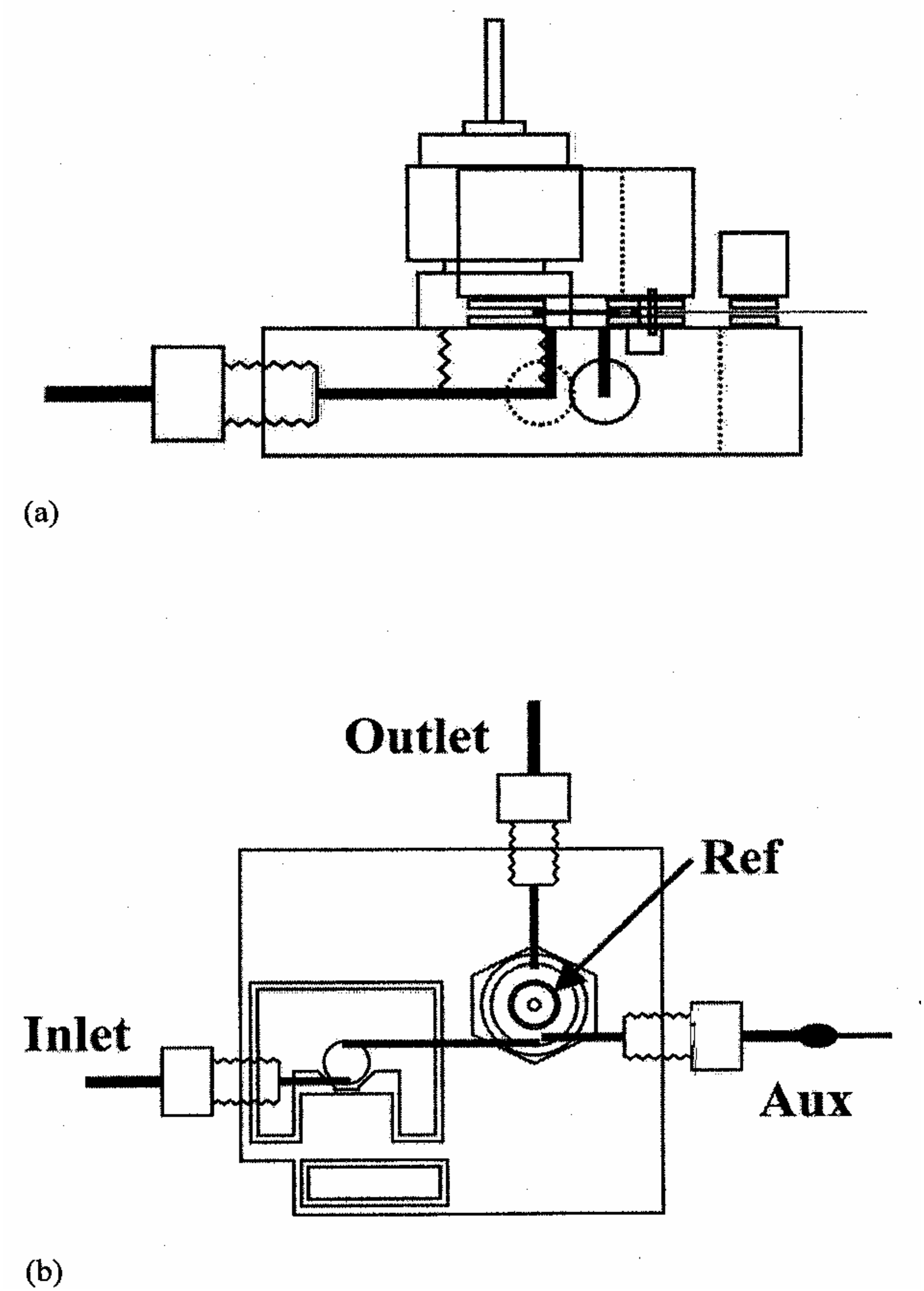
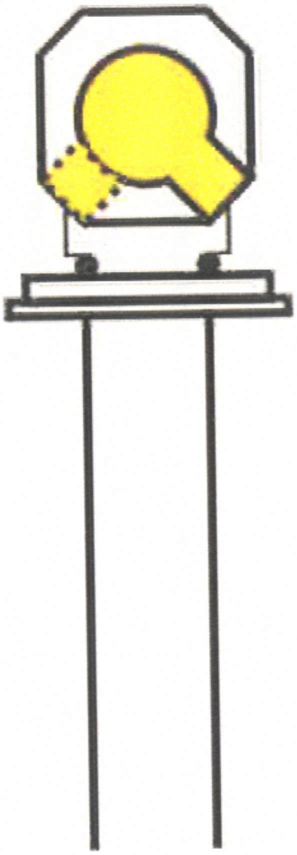


Fig 1.3



CHAPTER 2

FLOW CELL EQCM STUDY OF HGTE VIA EC-ALE

Jayaraju, N. and J.L.Stickney. To be submitted to *Analytical chemistry*.

Abstract

Compound semiconductors (HgSe, HgTe and Superlattice HgTe/CdTe) are important materials for optoelectronic applications, such as blue/green lasers, photovoltaics and IR detector materials. HgTe was grown via electrochemical atomic layer epitaxy (EC-ALE) for the first time. EC-ALE 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 layer-by-layer. EC-ALE allows better control of thin films growth, and control over composition and morphology, resulting in higher quality films. Best deposits were formed using Hg and Te deposition potentials of 0.40 V and -0.35 V, respectively, and using a Te stripping potential at -0.70 V. A flow cell electrochemical quartz crystal microbalance (EQCM) was used to study the optimum deposition conditions of HgTe to better understand the deposition process.

Introduction

Mercury Telluride is an II-VI compound semiconductor, which finds applications in the development of Mer Cad Tel ($Hg_{(1-x)}Cd_xTe$) IR detector material [1, 2]. HgTe has been grown by a variety of techniques such as molecular beam epitaxy (MBE) [3, 4], flash evaporation [5] and ALE [6]. Such techniques are generally carried out in gas or vacuum phase, using high purity precursors, at high temperatures. However, the ultra high vaccum requirements make operation very expensive.

Electrochemical Atomic Layer Epitaxy (EC-ALE) is a technique for electrodepositing nanofilms, and has been used most extensively to form compound semiconductors. EC-ALE is the electrochemical analog of ALE [7, 8] and ALD [9-11], all methods based on the use of surface limited reactions to form deposits with atomic layer control. The advantages of these methodologies are that they can be used to control deposition at the atomic level. The method breaks the deposition process into a sequence of individually controllable steps, thus greatly improving the ability to optimize a process. A number of II-VI [12-17] and III-V [18-20] compounds have been deposited via EC-ALE.

In electrochemical studies, surface limited reactions are generally referred to as under potential deposition (UPD). UPD is used in EC-ALE where one element electrodeposits on another, at a potential prior to (under) the potential at which the first element deposits on to itself, to obtain atomic layer by atomic layer growth [21-23].

When HgTe was grown via EC-ALE, oxidative charges were obtained not reduction at Hg deposition potentials. The negative coverages obtained from coulometry for Hg might probably be due to the simultaneous oxidation of Te at Hg deposition potentials. Faraday’s law should allow calculation of deposited amounts. Questions concerning the deposition mechanism were investigated using the EQCM flow cell.

Electrochemical quartz crystal microbalance (EQCM) has been constructed in this laboratory to study the deposition of compound semiconductors via EC-ALE. EQCM [24-27] is an in-situ mass sensing device, which is capable of measuring very small mass changes on the electrode surface. When mass is deposited on the EQCM electrode, a frequency change is observed [28]. The linear relationship between frequency change and mass change is described by the Sauerbrey equation:

$$\mathbf{\Delta F = (2nf_0^2 / \sqrt{\mu\rho})\, \Delta m = -C_f\Delta m}$$

ΔF: Measured frequency change (Hz)

Δf_0: Resonance frequency of the quartz crystal (Hz)

Δm: Change in mass per unit area (g cm^{-2})

ρ: Density of quartz ((2.648 g cm^{-3})

μ: Shear modulus of quartz (2.947 x 10^{11} g cm^{-1} s^{-2})

n: Number of the harmonic at which the crystal is driven

C_f: Sensitivity factor (Hz cm^2 g^{-1}).

The negative sign in the Sauerbrey equation indicates that Δf decreases when mass is added on the QCM electrode and vice versa. The problems encountered during the electrodeposition of HgTe using EC-ALE was studied using the flow cell EQCM.

Experimental

The electrochemical flow cell deposition system used for thee studies have been previously described [29-31]. Optimum conditions were studied in this automated flow cell system, consisting of a flow cell EQCM, a series of solution containers, a distribution valve, a potentiostat, an oscillator unit, and a frequency counter. Helium gas (99.99 %) was used to purge the solution to remove the dissolved oxygen. The solutions were pushed in to the cell from the pressurized 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 an 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 Δf 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.

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. H_2SO_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 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). The efficiency of the faradaic reactions for Ag was essentially 100 %. The integrated current (charges), plotted against measured Δf 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 4.58ng cm^{-2} Hz^{-1}.

The solutions used were 0.2 mM HgO, pH 2 and 0.2 mM TeO_2, pH 4, and both contained 0.5 M Na_2SO_4. The blank solution contained only the 0.5 M Na_2SO_4, at pH 4. Solution pH was adjusted using H_2SO_4. Water used for solutions was supplied from a Nanopure water filtration system (Barnstead, Dubuque, IA) attached to the house DI water system. Chemicals were reagent grade or better. For calibration of the EQCM, a 2 mM $AgNO_3$ in 0.1 M $HClO_4$ was used. De-ionized water (18.0 M. cm), obtained from a NANOpure UV ultrapure water system (Barnstead International, Dubuque, IA), and was used to prepare all solutions. The 50 mM $HClO_4$ (J.T.Baker) was used for electrochemical cleaning of the EQCM electrode by switching between +1.30 and –0.30 V for three cycles of oxidation and reduction of the gold electrode.

Results and discussion

The deposition potentials initially chosen for Hg and Te were obtained from cyclic voltammetric data for Au electrodes in the Hg and Te solutions [16]. An EC-ALE cycle was investigated in order to optimize the deposition of HgTe. During the optimization of HgTe, there were a lot of questions concerning the coverage for Hg and the possible redox replacement of Te by Hg.

The following EC-ALE cycle was then chosen (Figure 2.1) for HgTe deposition. Before deposition, the EQCM electrode was cleaned according to the procedure described in the experimental section. The deposition started with the blank being pumped in to the cell for 300s to stabilize the quartz crystal. Te solution was then rinsed into the cell for 17 s at -0.35 V. The cell was then flushed with blank solution for 7 s at -0.35 V, at which point, the potential was then changed to -0.70 V for 3 s. After which, Hg solution was flushed through the cell for 17 s at 0.40, to deposit. This was followed by another blank rinse at 0.40 V for 7 s.

Questions concerning this cycle and the deposition mechanism were investigated using an EQCM (Electrochemical quartz crystal microbalance) flow cell. Some aspects of the deposition process in the EQCM flow cell differed from those in the standard flow cell hardware. For instance, experience has shown that the EQCM flow cell worked best if solution was continuously pumped through the cell, no static deposition was used, however a much lower flow rate was used (6 mL/min). Overall, use of continuous flow in the EQCM did not appear to significantly change the resulting deposit. The optimal EC-ALE program was repeated for 5 cycles, with the fifth cycle shown in Figure 2.2. The cycle to cycle variations were minimal and predictable, allowing conclusions to be drawn concerning the changes in mass between cycles. However, within a cycle, variations in frequency were a function of a number of variables besides the masses of electrodeposited atomic layers. For instance the mass for reversibly adsorbed electrolyte may increase, upon adsorption, or decrease, upon desorption, the observed mass changes in a given solution. This results in statements concerning mass changes observed within a cycle to be educated guesses. On the other hand, mass changes from the same points in one cycle to the next are an accurate measure of the mass change for a cycle.

The results shown in Figure 2.2 indicate Te coverage of 2.62 ML from mass and 1.79 ML from coulometry. The Hg coverage was 2.18 ML and -0.39 ML from mass and charge respectively. The negative Hg coverage, based on charge indicates that a net oxidative charge was passed during Hg deposition. The question is then what is being oxidized if Hg^{2+} ions are being reduced? Te may be vulnerable to oxidation at such a positive potential. This then leads to the question of a redox replacement reaction, where deposited Te is traded for Hg at this potential. An experiment devised to investigate this question involved first deposition of three cycles of HgTe, followed by a blank rinse for 17 s at the Hg deposition potential (0.40 V). An oxidation current was observed (Figure 2.3), which appears to indicate that Te was being oxidized in the absences of Hg^{2+} ions, as there was nothing else in the solution to oxidize. It was also important to determine the length of time required to oxidize all of the excess Te at Hg deposition potential. So, again the same experiment was performed, but instead of flowing blank for 17 s, a 10 minute rinse was performed (Figure 2.4), which suggests that it takes about 3 minutes to strip excess Te from the deposit surface. The net Te coverage was 0.42 ML, on top of the previously deposited Hg layer, very close to the ideal Te coverage of 0.44 ML.

The next question is whether Hg^{2+} was replacing Te by a redox replacement reaction. In order to study this problem, three cycles of HgTe were deposited using the deposition program, followed by rinsing with the Hg^{2+} solution for 1 minute at open circuit (Figure 2.5). The mass of the electrode appeared to have increased but not enough to suggest a redox replacement of Te taking place. If there was an actual replacement taking place then the deposited Te would be oxidizing into $HTeO_2^+$, giving out four electrons to Hg^{2+} ions to deposit. So for every Te atom being oxidized, two Hg atoms would be reducing. The mass change in terms of frequency change of the quartz crystal for this reaction would be around 537.8 Hz. This kind of mass change was not observed by the EQCM experiment (137.0 Hz). Moreover, a 3 s blank rinse after the open circuit Hg solution rinse resulted in a corresponding decrease in electrode mass, suggesting desorption of adsorbed Hg ions. These results suggest that Te was not replaced by Hg at open circuit.

From the experiment shown in Figure 2.4, it was found that 3 minute was required to strip all excess Te. The same experiment was repeated, but instead of blank solution flowing for 10 minutes, a 3 minute rinse was done to remove excess Te. Hg solution was then flowed and the potential was switched to +0.400V and a reductive charge was observed for Hg deposition.

Conclusion

HgTe grown via EC-ALE was studied was studied using a EQCM. The optimum deposition of HgTe was formed using Hg and Te deposition potentials of 0.40 V and -0.35 V, respectively, and using a Te stripping potential at -0.70 V. Studies using EQCM helped us to better understand the deposition process. It showed that some of the Te in each cycle was oxidatively stripped upon switching the potential from -0.350V to the Hg deposition potential, +0.400V. It was also proved that a redox replacement reaction was not taking place; Te was not exchanged for Hg.

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Figure Captions

Figure 2.1: Optimal deposition program for HgTe deposition.

Figure 2.2: Current-time profile during HgTe deposition using optimal deposition ` program by EQCM (5th cycle).

Figure 2.3: EQCM experiment showing oxidation of Te at Hg deposition potential of 0.40V.

Figure 2.4: EQCM experiment showing the time dependence of Te oxidation at Hg Deposition potential (0.40V).

Figure 2.5: EQCM experiment to determine redox exchange of Te with Hg at open circuit.

Figure 2.6: EQCM experiment to show complete oxidation of bulk Te and reductive charge for Hg deposition.

Fig 2.1

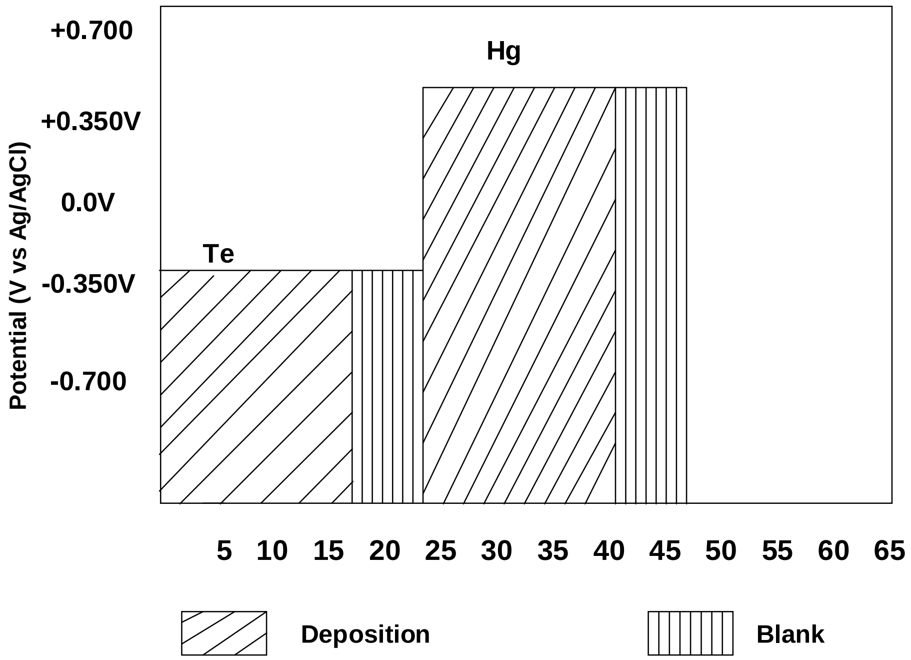

+0.700
Hg
+0.350V
0.0V
Te
-0.350V
-0.700
Potential (V vs Ag/AgCl)
5
10
15
20
25
30
35
40
45
50
55
60
65
Deposition
Blank

Fig 2.2

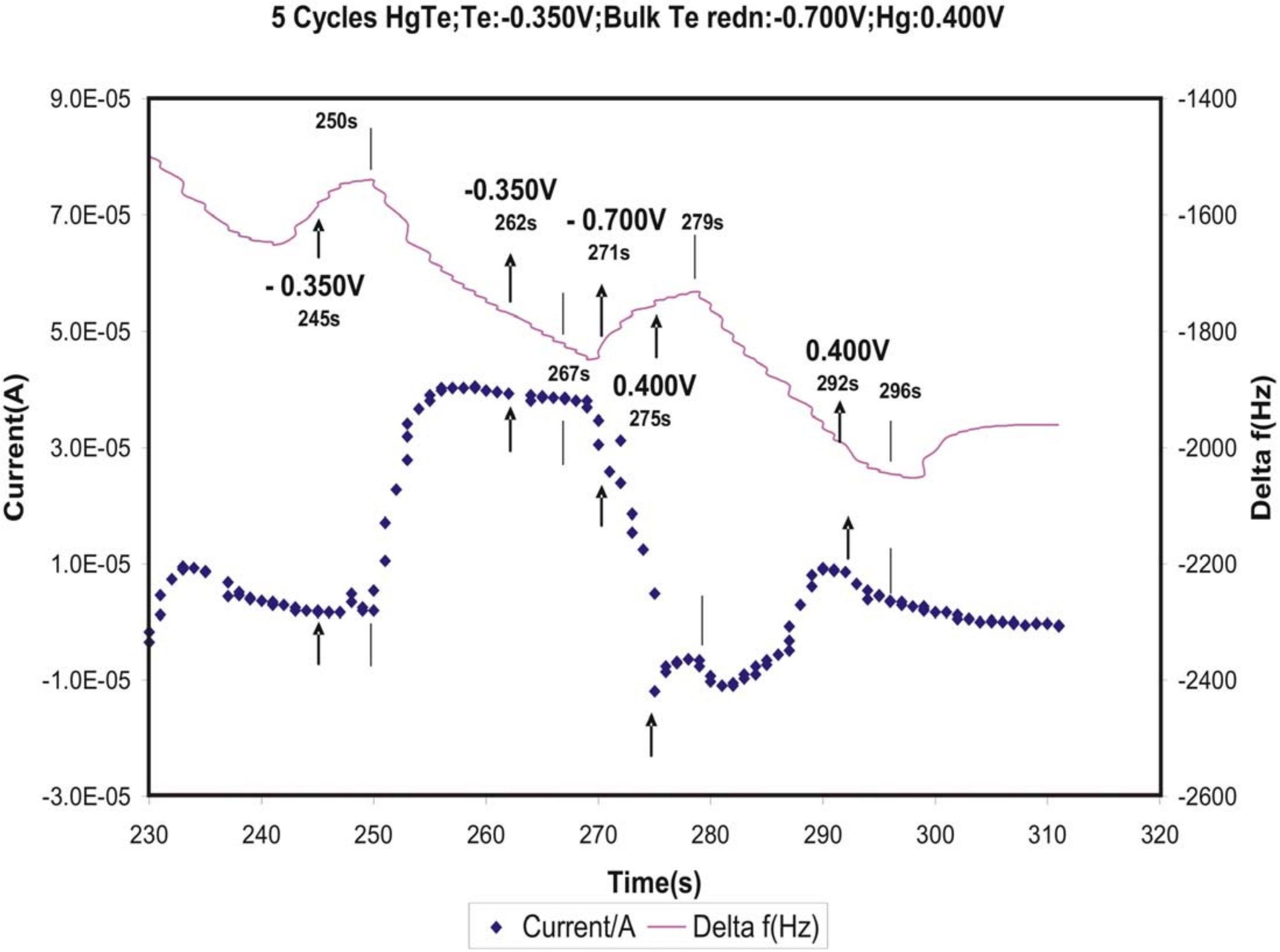

5 Cycles HgTe;Te:-0.350V;Bulk Te redn:-0.700V;Hg:0.400V
Current(A)
Delta f(Hz)
Time(s)
9.0E-05
7.0E-05
5.0E-05
3.0E-05
1.0E-05
-1.0E-05
-3.0E-05
-1400
-1600
-1800
-2000
-2200
-2400
-2600
230
240
250
260
270
280
290
300
310
320
250s
-0.350V
262s
- 0.700V
279s
271s
- 0.350V
245s
267s
0.400V
275s
0.400V
292s
296s
◆ Current/A
Delta f(Hz)

Fig 2.3

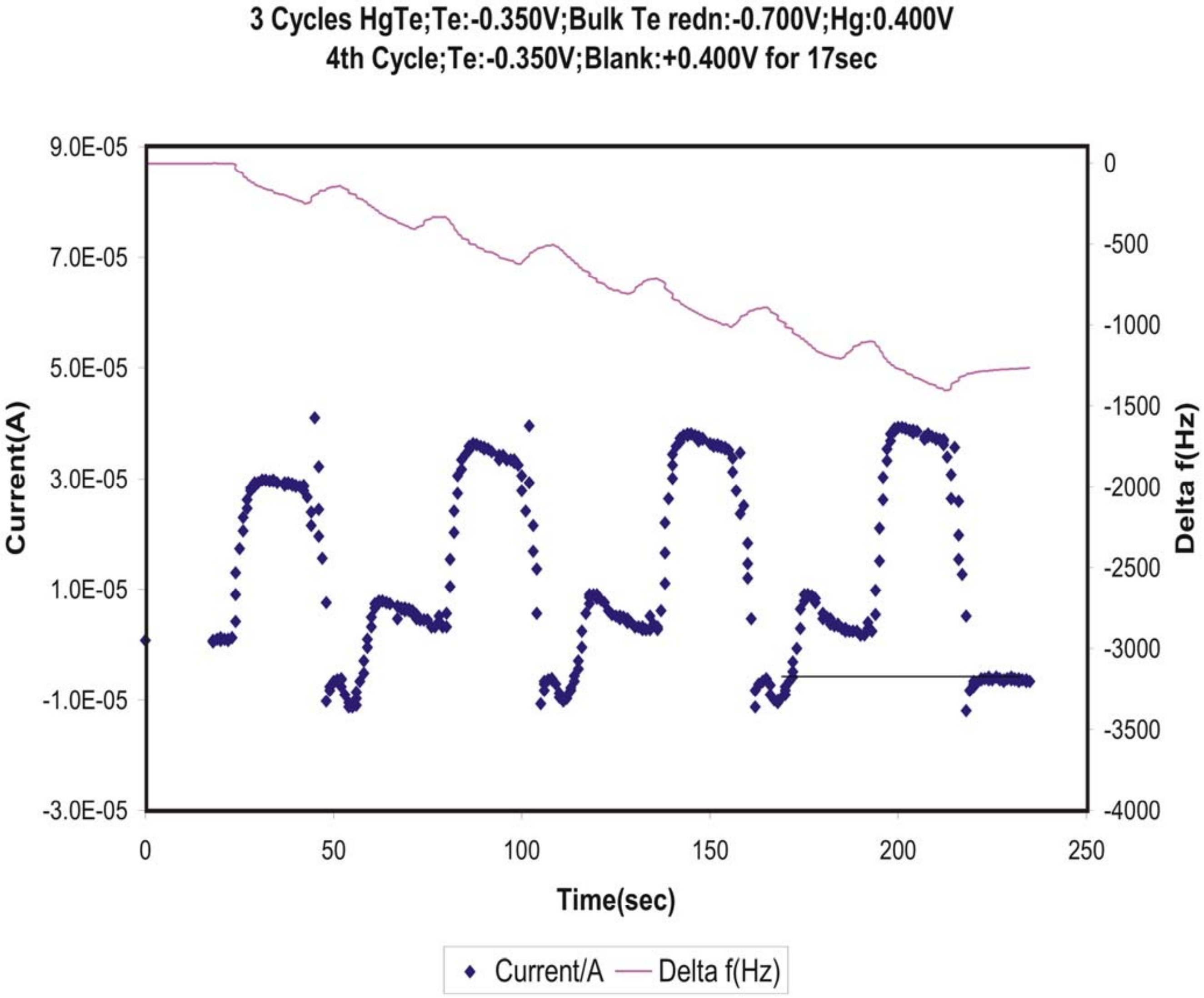

3 Cycles HgTe;Te:-0.350V;Bulk Te redn:-0.700V;Hg:0.400V
4th Cycle;Te:-0.350V;Blank:+0.400V for 17sec
Current(A)
9.0E-05
7.0E-05
5.0E-05
3.0E-05
1.0E-05
-1.0E-05
-3.0E-05
Delta f(Hz)
0
-500
-1000
-1500
-2000
-2500
-3000
-3500
-4000
0
50
100
150
200
250
Time(sec)
◆ Current/A
Delta f(Hz)

Fig 2.4

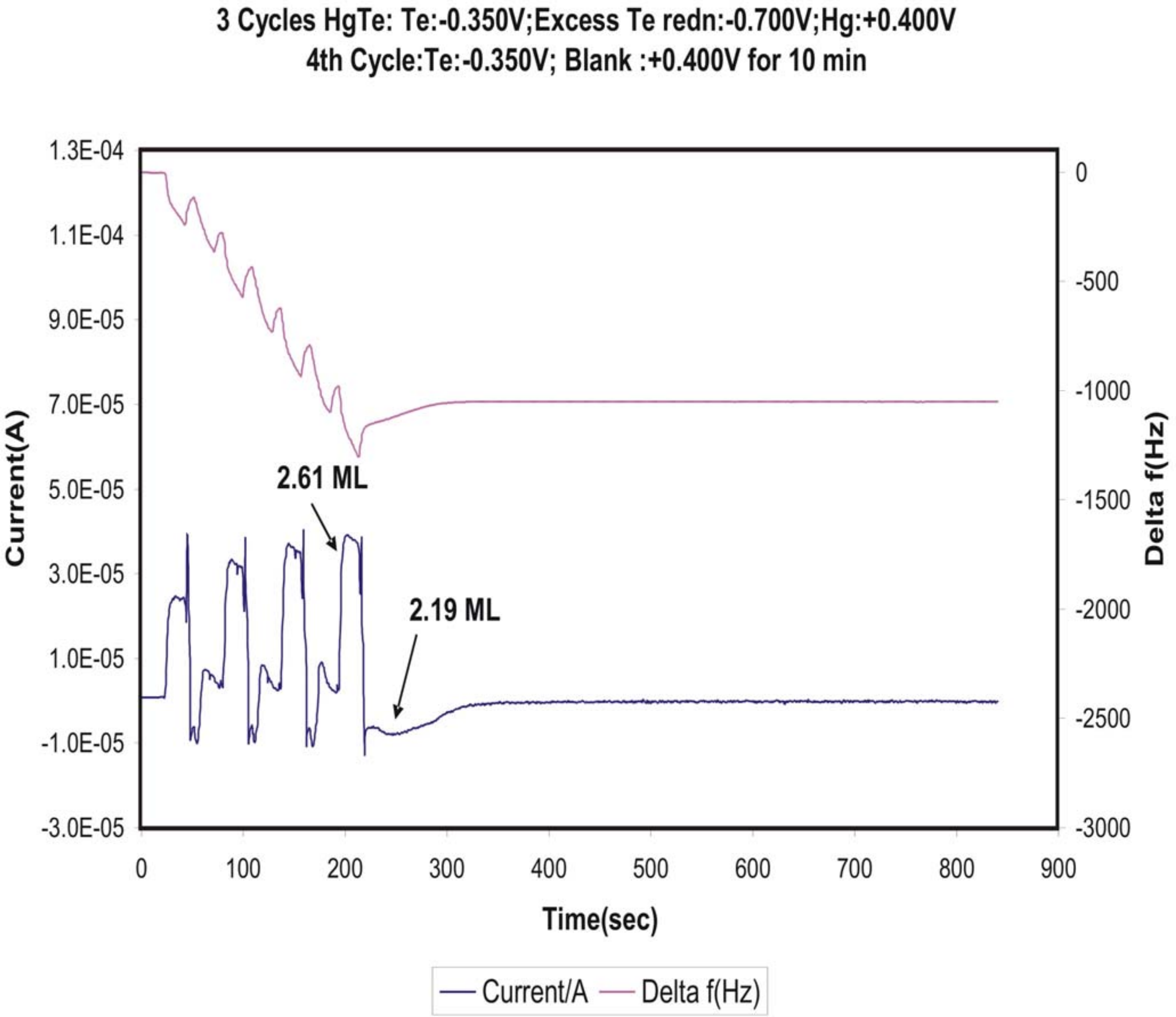

3 Cycles HgTe: Te:-0.350V;Excess Te redn:-0.700V;Hg:+0.400V
4th Cycle:Te:-0.350V; Blank :+0.400V for 10 min
Current(A)
1.3E-04
1.1E-04
9.0E-05
7.0E-05
5.0E-05
3.0E-05
1.0E-05
-1.0E-05
-3.0E-05
Delta f(Hz)
0
-500
-1000
-1500
-2000
-2500
-3000
2.61 ML
2.19 ML
0
100
200
300
400
500
600
700
800
900
Time(sec)
Current/A
Delta f(Hz)

Fig 2.5

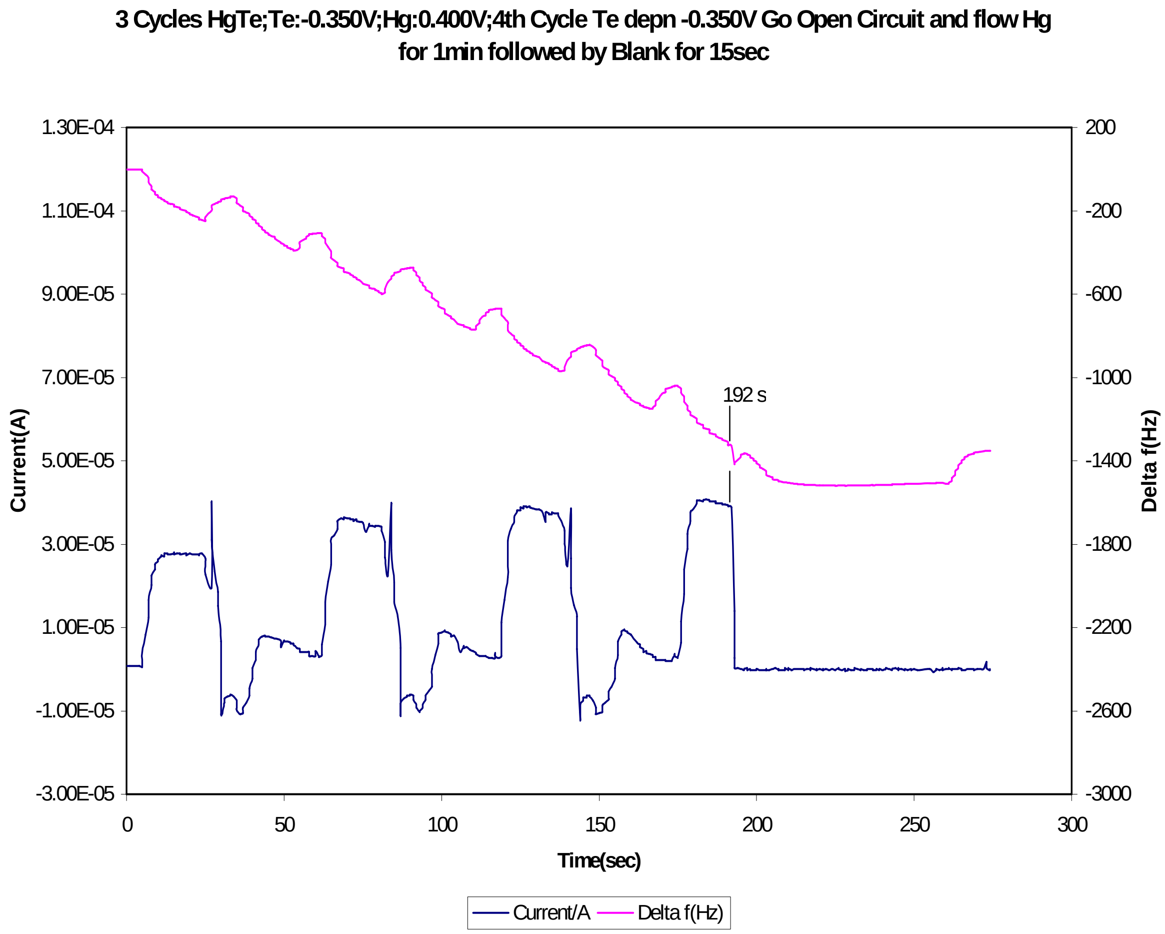
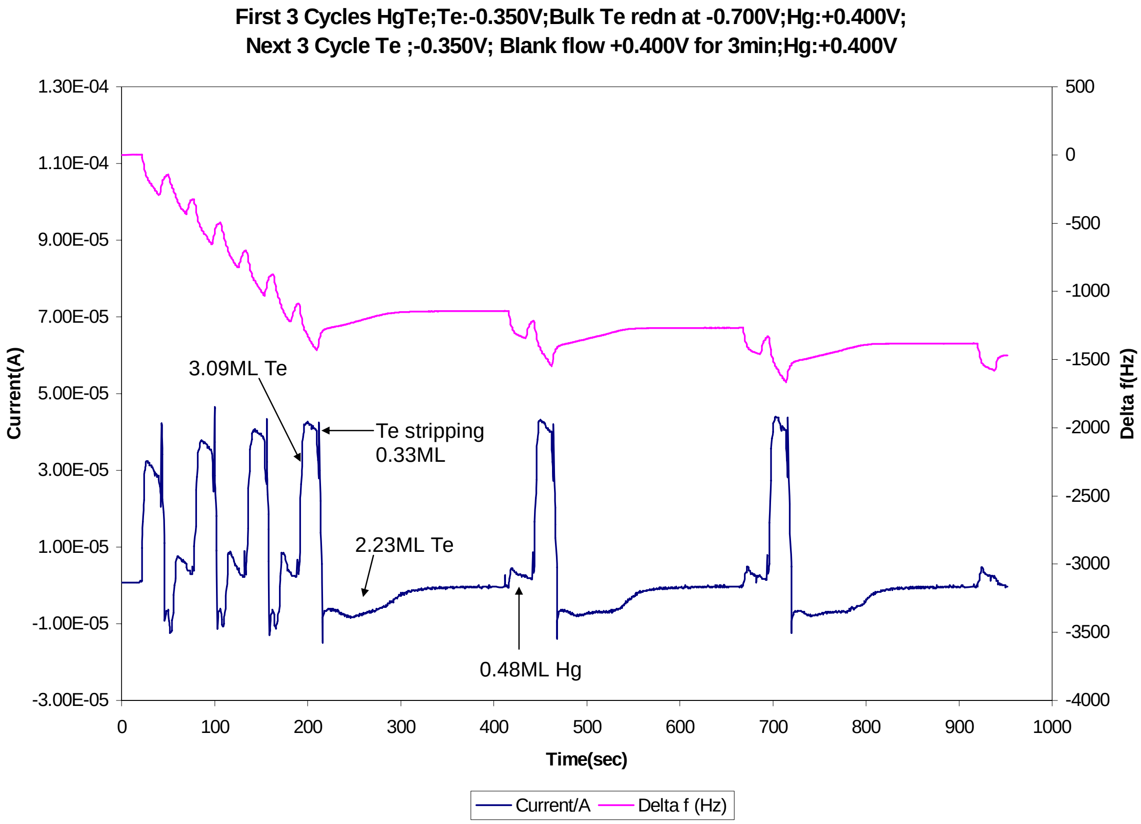

3 Cycles HgTe;Te:-0.350V;Hg:0.400V;4th Cycle Te depn -0.350V Go Open Circuit and flow Hg for 1min followed by Blank for 15sec
1.30E-04
1.10E-04
9.00E-05
7.00E-05
5.00E-05
3.00E-05
1.00E-05
-1.00E-05
-3.00E-05
Current(A)
200
-200
-600
-1000
-1400
-1800
-2200
-2600
-3000
Delta f(Hz)
192 s
0
50
100
150
200
250
300
Time(sec)
Current/A
Delta f(Hz)

Fig 2.6


First 3 Cycles HgTe;Te:-0.350V;Bulk Te redn at -0.700V;Hg:+0.400V;
Next 3 Cycle Te ;-0.350V; Blank flow +0.400V for 3min;Hg:+0.400V
Current(A)
1.30E-04
1.10E-04
9.00E-05
7.00E-05
5.00E-05
3.00E-05
1.00E-05
-1.00E-05
-3.00E-05
Delta f(Hz)
500
0
-500
-1000
-1500
-2000
-2500
-3000
-3500
-4000
0
100
200
300
400
500
600
700
800
900
1000
Time(sec)
3.09ML Te
Te stripping
0.33ML
2.23ML Te
0.48ML Hg
Current/A
Delta f (Hz)

CHAPTER 3

FLOW CELL EQCM STUDY OF CDTE/HGTE SUPERLATTICE VIA ELECTROCHEMICAL ATOMIC LAYER DEPOSITION (ALD)

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Abstract

Electrochemical atomic layer deposition (ALD) is a technique used to electrodeposit thin films of compound semiconductors. It is the electrochemical analog of atomic layer epitaxy (ALE) and atomic layer deposition (ALD). MCT films were grown via electrochemical ALD. ALD 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 layer-by-layer. Electrochemical atomic layer deposition (ALD) allows better control of thin films growth, and control over composition and morphology, resulting in higher quality films. A flow cell electrochemical quartz crystal microbalance (EQCM) was used to study the optimum deposition conditions of MCT and to better understand the deposition process.

Introduction

$Hg_{(1-x)}Cd_xTe$ an important II-VI compound semiconductor [1] finding applications in the development of IR detector materials and photovaltaics. MCT has been grown by a variety of techniques such as MBE [2-4], MOCVD [5, 6] and MOVPE [7]. Such techniques are generally carried out in gas or vacuum phase, using high purity precursors and at high temperatures. However, the vaccum requirements make operation expensive.

Electrochemical atomic layer deposition (ALD) is the electrochemical analog of ALE [8, 9] and ALD [10, 11], all methods based on the use of surface limited reactions to form deposits with atomic layer control. A number of II–IV compounds such as CdS, CdTe, HgSe, and HgTe [12-15], III–V compounds such as InAs and InSb as well as PbSe, Bi_2Te_3, and Sb_2Te_3 [16-22] have been successfully deposited by Electrochemical

ALD. The advantages of these methodologies are that they can be used to control deposition at the atomic level. The method breaks the deposition process into a sequence of individually controllable steps, thus greatly improving the ability to optimize a process.

In electrochemical studies, surface limited reactions are generally referred to as underpotential deposition (UPD) [23-25]. UPD is a phenomenon where in one element electrodeposits on another, at a potential prior to (under) the potential at which the first element deposits on to itself. Electrochemical ALD involves the sequential electrodeposition of atomic layers of elements, to form nanofilms of materials using underpotentials.

MCT has proven to be significantly more difficult to form using electrochemical ALD than either CdTe or HgTe, because of the large difference in stability between Hg and Cd, nearly a volt. A flow cell electrochemical quartz crystal microbalance (EQCM) was used to study the deposition processes. EQCM is an in-situ 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:

$$\mathbf{\Delta F = (2nf_0^2 / \sqrt{\mu\rho})\ \Delta m = -C_f\Delta m}$$

ΔF: Measured frequency change (Hz)

Δf_0: Resonance frequency of the quartz crystal (Hz)

Δm: Change in mass per unit area (g cm-2)

ρ: Density of quartz ((2.648 g cm-3)

μ: Shear modulus of quartz (2.947×10^{11} g cm^{-1} s^{-2})

n: Number of the harmonic at which the crystal is driven

C_f: Sensitivity factor (Hz cm^2 g^{-1}).

The negative sign in the Sauerbrey equation indicates that Δf decreases when mass is added on the QCM electrode and vice versa. EQCM is used to study MCT using Electrochemical ALD.

Experimental

The electrochemical flow cell deposition system used for these studies has been previously described. Deposition was carried out in an automated flow cell system consisting of a flow cell EQCM, a series of solution containers, a distribution valve, a potentiostat, an oscillator unit, and a frequency counter. Helium gas (99.99 %) was used to purge the solution, to remove dissolved oxygen and also to build pressure inside the bottles. The solutions were pushed in to the cell from the pressurized bottles. The details of the deposition system were described in detail in previous chapters.

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). The crystals were cleaned in conc. H_2SO_4 for five minutes in an ultrasonic cleaner (Cole- Parmer, Vernon Hills, IL). De-ionized water was used to thoroughly rinse the crystals .They were then dried with N_2 and assembled into the flow cell EQCM, described in the earlier chapters. The EQCM was calibrated using Ag electrodeposition using cyclic voltammetry. A cyclic voltammogram was obtained in the potential range of +0.85 to +0.10 V under static conditions. The integrated current (charges) plotted against measured Δf values, resulted in straight lines, and a linear regression analysis was used to fit the data. The average calibration constant was determined to be 4.58ng cm^{-2} Hz^{-1} (From the slope).

The solutions used were 0.2 mM HgO, pH 2, 0.2 mM TeO_2, pH 4, 0.5 mM $CdSO_4$ pH 5 and all contained 50 mM Na_2SO_4 supporting electrolyte. The blank solution contained only the 50 mM Na_2SO_4, at pH 4. Solution pH was adjusted using H_2SO_4. Water used for solutions was supplied from a Nanopure water filtration system (Barnstead, Dubuque, IA) attached to the house DI water system. Chemicals were reagent grade or better. For calibration of the EQCM, a 2 mM $AgNO_3$ in 0.1 M $HClO_4$ was used. De-ionized water (18.0 M. cm), obtained from a NANOpure UV ultrapure water system (Barnstead International, Dubuque, IA), and was used to prepare all solutions. The 50 mM $HClO_4$ (J.T.Baker) was used for electrochemical cleaning of the EQCM electrode by switching between +1.30 and –0.30 V for three cycles of oxidation and reduction of the gold electrode.

The Electrochemical ALD program used to deposit MCT involved the separate deposition of HgTe and CdTe monolayers. The following ALD cycle was then chosen for HgTe deposition. Before deposition, the EQCM electrode was cleaned according to the procedure described in the experimental section. The deposition starts with the blank being pumped in to the cell for 300s to stabilize the quartz crystal. Te solution was then rinsed into the cell for 17s at -0.35 V. The cell was then flushed with blank solution for 7s at -0.35 V, at which point, the potential was then changed to -0.70 V for 3s. After which, Hg solution was flushed through the cell for 17s at 0.40, to deposit. This was followed by another blank rinse at 0.40 V for 7s.

CdTe depositions started with Cd solution being flushed into the cell for 17s at -0.65V. Blank solution was then flushed through the cell for 7s. Te was then pumped in for 17s at -0.35V followed by a blank rinse for 7s and bulk Te stripping at -0.70Vs for 11s.

Results and discussion

MCT has proven to be significantly more difficult to form using electrochemical ALD than either CdTe or HgTe, because of the large difference in stability between Hg and Cd, nearly a volt. MCT was studied with the flow deposition system previously described. Optimization studies were carried in a flow cell system. The system used was previously described. There were questions concerning the negative coverage for Hg and Cd oxidation at Hg deposition potential, the redox replacement of Cd by Hg. To better understand the deposition program and to answer these questions about the deposition mechanism, an electrochemical quartz crystal microbalance (EQCM) flow cell system was employed. The program using the EQCM differed slightly from that used to form the deposits. EQCM experiments were performed by continuously flowing the solutions. Experience has shown that stopping flow with the EQCM resulted in dramatic changes in the frequency, while continuous flow through the cell does not show this effect, at reasonable flow rates. No problems of this type were observed using 6 mL/min. Figure 3.1 shows the current-time response and the frequency change during the deposition of 3 cycles of CdTe followed by 3 cycles of HgTe. Of particular note is the fact that no reduction was evident during the Hg^{2+} deposition steps. In fact, an oxidative current was present. However, from EPMA, it was clear that Hg was deposited.

The problem is that at the potentials needed to deposit Hg UPD, Cd in CdTe was not very stable. Apparently, some of the Cd deposited in previous CdTe cycles was oxidatively stripped when the potential was switched to 0.40 V, to deposit Hg. To substantiate this conclusion, 3 cycles of CdTe were deposited, followed by a blank rinse at 0.40 V. Oxidation current was observed (Figure 3.2) as well as a mass decrease, indicating loss of Cd from the surface, while the potential was maintained at 0.40 V. In addition, redox replacement of Cd by Hg^{2+} was likely under these conditions, where some charge for Hg^{2+} reduction came directly from oxidation of Cd to Cd^{2+}, a fairly probable event given the difference in the potentials used in the present study for Hg and Cd deposition, 0.40 V and -0.65 V respectively. To better understand this process, five cycles of CdTe were formed using the same deposition program (Figure 3.3), but instead of flowing Hg^{2+} solution at 0.40 V, it was introduced at open circuit for 1 minute (Figure 9). The mass of the electrode increased, even in the absence of potential control, as heavy Hg atoms replaced lighter Cd atoms. The mass loss, evident at the end (Figure 3.3), resulted from a blank rinse. Anytime the solution flowing over the EQCM electrode changes, some mass change is expected, given that reversibly adsorbed species in equilibrium with the old solution are exchanged for new species which adsorbs in equilibrium with new solution. This makes assignment of mass changes from step to step difficult, but allows mass changes from equivalent points in different cycles to be assigned. If all the Cd deposited in the five cycles of CdTe were replaced by Hg, a mass change of 450 Hz would be expected. The measured mass change was 480 Hz. That is, given sufficient time, all the Cd was exchanged at open circuit in the Hg^{2+}solution, for Hg. This raises the question of why was there any Cd present in the deposits formed in this study? There were two significant differences between the program and instrumentation used for the EQCM experiment shown in Figure 3.3 and those used to form the deposits in the flow cell system: longer times and continuous flow were used for the EQCM study. During depositon in the flow cell system, all the Cd was not replaced because only 15 second was allowed for exchange, and there was no flow during the deposition, limiting the redox replacement of Cd for Hg. The effect of holding the potential at 0.40 V is not clear. Obviously, 0.40 V must have been positive of the OCP, given that oxidative current was observed. It would then be expected that Cd oxidation would accelerate, while Hg deposition might slow down. The net result over the 15 seconds used for Hg deposition was that some Cd was replaced or oxidized but not all, and Hg did deposit.

Conclusion

The Electrochemical ALD cycle used to grow MCT was studied using a flow cell EQCM to better understand the deposition process. These studies showed that the Cd deposited in CdTe was oxidatively stripped, upon switching the potential to +0.40V for Hg deposition. It also showed that a redox replacement reaction takes place and some Cd was exchanged for Hg.

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Figure Captions

Figure 3.1: Current-Time-Δf profile of HgCdTe deposition by EQCM.

Figure 3.2: EQCM experiment showing oxidation of Te at Hg deposition potential of 0.40V.

Figure 3.3: EQCM experiment to determine redox exchange of Cd with Hg at open circuit.

Fig 3.1

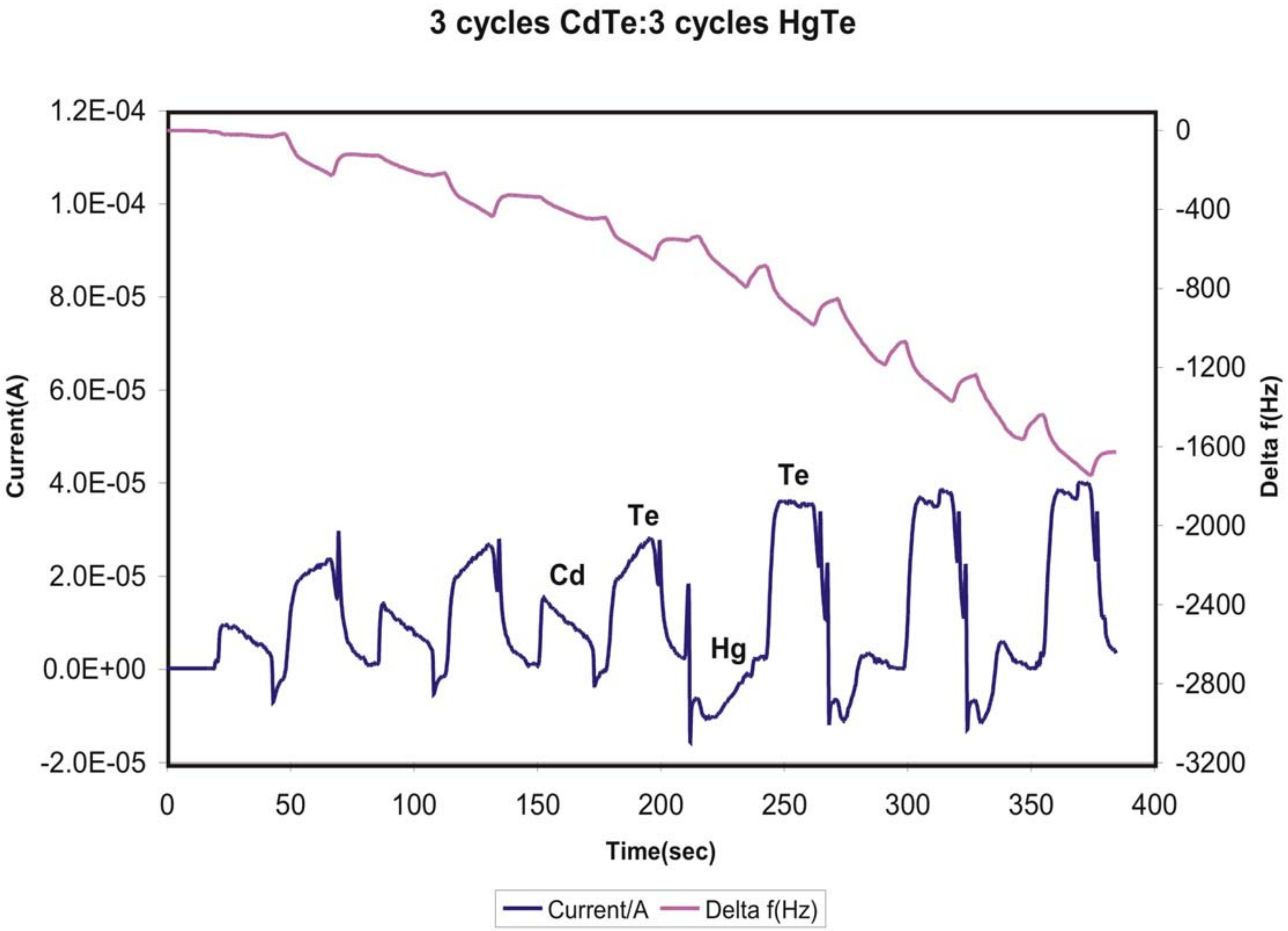

3 cycles CdTe:3 cycles HgTe
Current(A)
1.2E-04
1.0E-04
8.0E-05
6.0E-05
4.0E-05
2.0E-05
0.0E+00
-2.0E-05
Delta f(Hz)
0
-400
-800
-1200
-1600
-2000
-2400
-2800
-3200
Time(sec)
0
50
100
150
200
250
300
350
400
Cd
Te
Hg
Te
Current/A
Delta f(Hz)

Fig 3.2

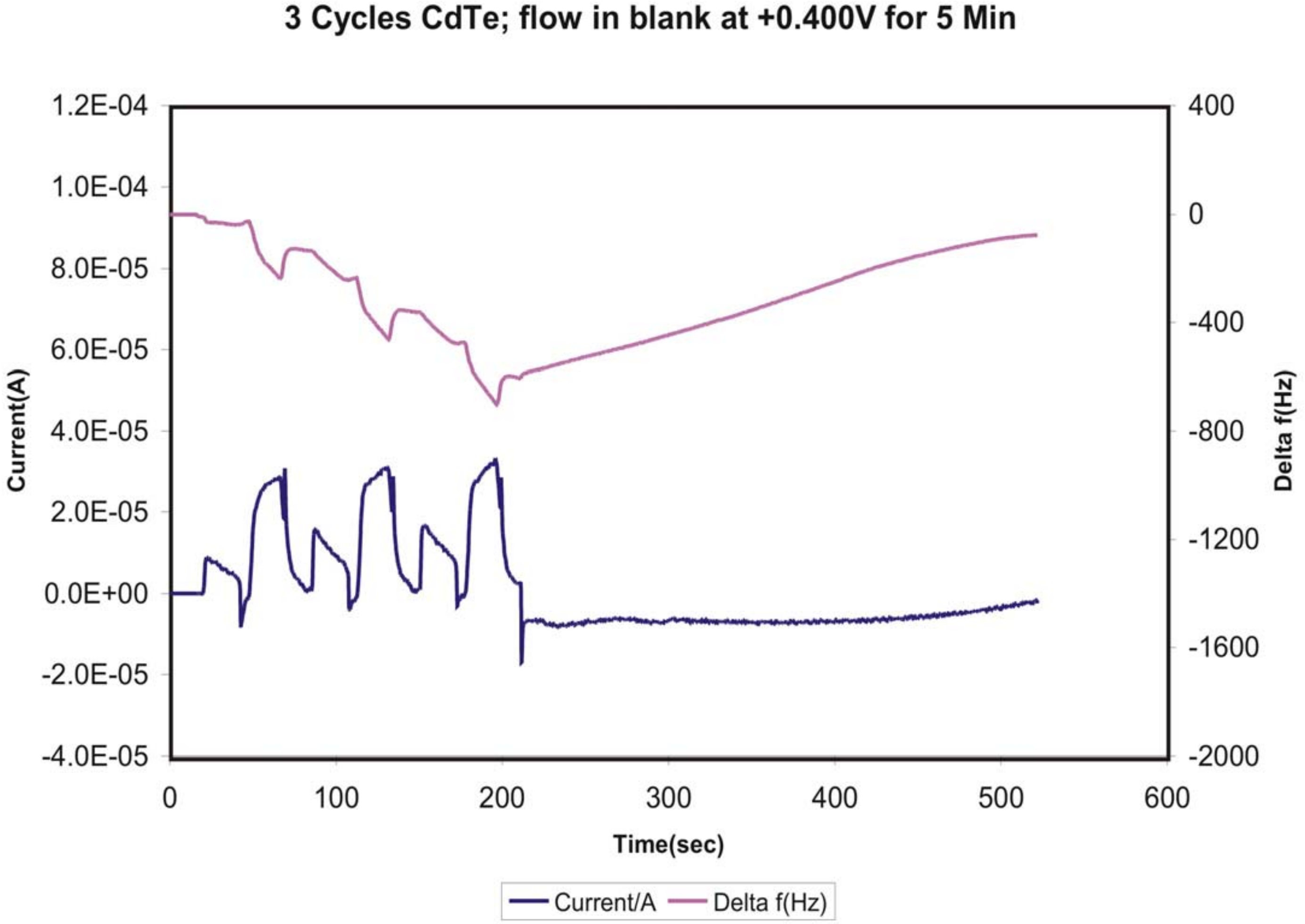
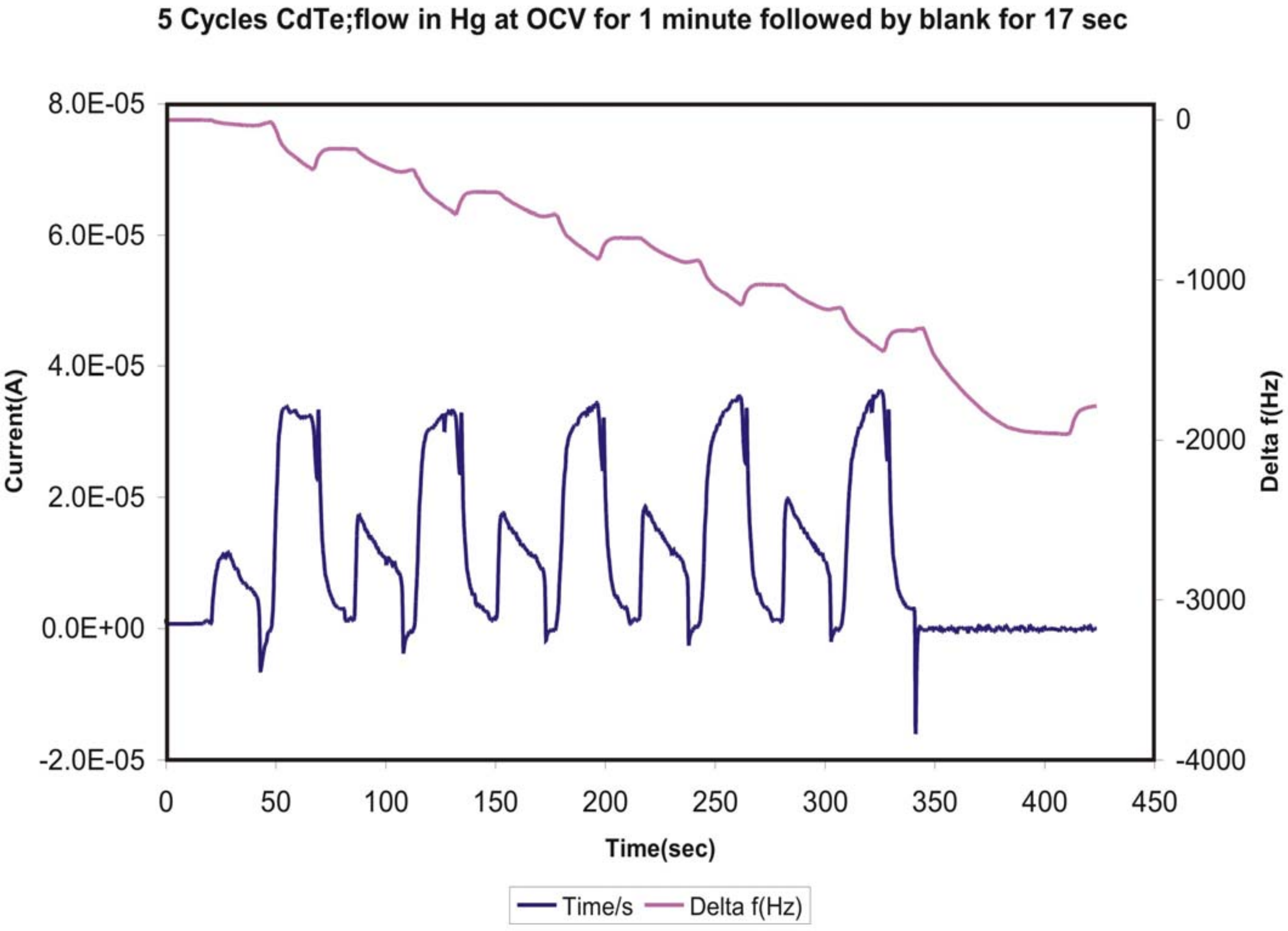

3 Cycles CdTe; flow in blank at +0.400V for 5 Min
1.2E-04
1.0E-04
8.0E-05
6.0E-05
4.0E-05
2.0E-05
0.0E+00
-2.0E-05
-4.0E-05
Current(A)
400
0
-400
-800
-1200
-1600
-2000
Delta f(Hz)
0
100
200
300
400
500
600
Time(sec)
Current/A
Delta f(Hz)

Fig 3.3


5 Cycles CdTe;flow in Hg at OCV for 1 minute followed by blank for 17 sec
Current(A)
8.0E-05
6.0E-05
4.0E-05
2.0E-05
0.0E+00
-2.0E-05
Delta f(Hz)
0
-1000
-2000
-3000
-4000
0
50
100
150
200
250
300
350
400
450
Time(sec)
Time/s
Delta f(Hz)

CHAPTER 4

EQCM STUDY OF CU THIN FILM ON GOLD BY ELECTROCHEMICAL ATOMIC LAYER DEPOSITION (ALD)

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Abstract

Nanofilms of Cu were grown on Au using under potential deposition and surface limited redox replacement (SLRR). Electrochemical ALD is a technique for the growth of metal and semiconductor nanofilms. UPD is a phenomenon where in one element deposits at a potential prior to that needed to deposit the element on itself. In a SLRR, an atomic layer of a less noble metal is replaced by an atomic layer of a more noble metal at Open Circuit. The first element can be thought of as a sacrificial atomic layer, limiting the number of electrons available for the replacing metal. As this reaction takes place at open circuit, coulometric data is not available to quantify the amount of the more noble metal deposited. EQCM was used to follow the mass changes during the growth of Cu nanofilms. A solution flow rate of 6.1 ml min^{-1} was used. For Cu film growth, Pb UPD was used to form the sacrificial metal atomic layer, and was deposited at -0.440V and replaced with copper at open circuit.

Introduction

Electrochemical Atomic Layer Deposition (ALD) is a technique that has been used to grow compound semiconductors. Recently this technique has been applied, by our group, to grow metal nanofilms of Cu and Pt. In general electrodeposition of metals takes place by nucleation and growth, which results in 3D growth. Electrochemical ALD has been developed to promote 2D growth of metal nanofilm. 2D growth of thin films results in better control over roughness, deposit thickness and may lead to epitaxial growth. Electrochemical ALD is an analog of Atomic Layer Epitaxy (ALE)[1, 2] and Atomic Layer Deposition (ALD)[3-5], both techniques designed to result in 2D growth.

In electrochemical studies, surface limited reactions are generally referred to as under potential deposition (UPD) [6-8]. UPD is a phenomenon where in one element electrodeposits on another, at a potential prior to (under) the potential at which the first element deposits on to itself. Electrochemical ALD [9-14] has been applied to grow compound semiconductors. It has recently been extended to grow metal thin films of Cu and Pt on Au. The focus of this group has been the application of Electrochemical ALD for the formation of semiconductors and metal nanofilms.

Surface limited redox replacement (SLRR) is a technique designed to grow metals layer by layer. SLRR has been studied by Brankovic and Adzic [15], Weaver [16] and Dimitrov [17]. Cu nanofilm formation has been studied using UHV-EC techniques by Stickney etal. [18]. An atomic layer of a less noble metal is deposited using UPD and then exposed to a solution containing ions of a more noble element, resulting in redox replacement of the less noble metal (sacrificial metal) to form an atomic layer of the more noble metal. The desired thickness of the metal films can be controlled by repeating the ALD cycles.

In the SLRR of Cu by Pb, Cu is more noble than Pb, and therefore Cu should replace Pb UPD spontaneously. The reaction that takes place during this process is as follows: $Pb^{0}_{UPD} + Cu^{2+} \rightarrow Pb^{2+} + Cu^{0}$. As this reaction takes place at open circuit, coulometric data is not available to quantify the amount of Cu deposited. EQCM was used to study the Cu coverage based on mass changes during the growth of Cu nanofilms.

A flow cell electrochemical quartz crystal microbalance (EQCM)[19-22] has been constructed in this laboratory and used to study deposition processes for the formation of compound semiconductors via Electrochemical ALD. As SLRR takes place at open circuit, coulometric data is not available to quantify the amount of the more noble metal deposited. EQCM was used to follow the mass changes during the growth of Cu nanofilms. 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:[23]

$$\boldsymbol{\Delta F = (2nf_0^2 / \sqrt{\mu\rho})\ \Delta m = -C_f\Delta m}$$

ΔF: Measured frequency change (Hz)

$\Delta f_{o:}$ Resonance frequency of the quartz crystal (Hz)

Δm: Change in mass per unit area (g cm^{-2})

ρ: Density of quartz (($2.648\ \text{g cm}^{-3}$)

μ: Shear modulus of quartz ($2.947 \times 10^{11}\ \text{g cm}^{-1}\ \text{s}^{-2}$)

n: Number of the harmonic at which the crystal is driven

$C_{f:}$ Sensitivity factor ($\text{Hz cm}^{2}\ \text{g}^{-1}$).

The negative sign in the Sauerbrey equation indicates that Δf decreases when mass is added on the QCM electrode and vice versa. This paper describes the application of a flow cell EQCM to study the growth of Cu nanofilm via Electrochemical ALD.

Experimental

The electrochemical flow cell deposition system used for these studies has been previously described. Deposition was carried out in an automated flow cell system consisting of a flow cell EQCM, a series of solution containers, a distribution valve, a potentiostat, an oscillator unit, and a frequency counter. Helium gas (99.99 %) was used to purge the solution to remove the dissolved oxygen and also to build pressures inside the bottles. The details of the deposition system were described in detail in the previous chapters.

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. H_2SO_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 N_2. The crystals were assembled into the flow cell EQCM, described above.

The EQCM was calibrated using Ag electrodeposition using cyclic voltammetry. A cyclic voltammogram was obtained in the potential range of +0.85 to +0.10 V under static conditions. The integrated current (charge) plotted against the measured value of Δf resulted in straight lines, and a linear regression analysis was used to fit the data. The average calibration constant was determined to be 4.58ng cm^{-2} Hz^{-1}. (From the slope)

The solutions used were 1 mM $Pb(ClO_4)_2$, pH~2 in 50 mM $HClO_4$,1 mM $CuSO_4$, pH~2 in 50 mM H_2SO_4.and 0.1mM KI in 50mM $HClO_4$. The blank solution contained only the 50 mM $HClO_4$, at pH~2. Water used for solutions was supplied from a Nanopure water filtration system (Barnstead, Dubuque, IA) attached to the house DI water system. Chemicals were reagent grade or better. Calibration of the EQCM is done using 2 mM $AgNO_3$ in 0.1 M $HClO_4$. The 50 mM $HClO_4$ (J.T.Baker) was used to clean the electrode before and after depositions.

Electrochemical cleaning of the EQCM electrode involved flow of a 50 mM $HClO_4$ solution continuously through the deposition cell at a constant flow rate of ~0.6mL min^{-1}. The potential was stepped between +1.30 and –0.30 V for three cycles of oxidation and reduction of the gold electrode, to remove any contaminants on the electrode.

Results and discussion

The deposition potential for Pb UPD was obtained from cyclic voltammetric data for Au electrodes in the Pb solution. In this study, -0.440V was used to study the SLRR of Pb by Cu, without an iodine rinse and with an iodine rinse in each cycle. Iodine was introduced in each cycle to promote electrochemical annealing. The electrochemical flow deposition system used for these studies has been previously described. The conditions were optimized using the flow cell system and the optimal deposition conditions were studied using a flow cell based EQCM.

Experience has shown that the EQCM flow cell worked best if solution was continuously flowed through the cell, no static deposition was used, however a much lower flow rate was used (6 mL/min). The optimal ALD program was repeated for 10 cycles, current and Δf were plotted as a function of deposition time. The cycle to cycle variations were minimal and predictable, allowing conclusions to be drawn concerning the changes in mass between cycles. However, within a cycle, variations in frequency were a function of a number of variables besides the masses of electrodeposited atomic layers. For instance, reversibly adsorbed electrolyte may increase the electrode upon adsorption, or decrease the mass upon desorption. This forces statements concerning mass changes observed within a cycle to be educated guesses. On the other hand, mass changes from the same points in one cycle to the next are an accurate measure of the mass change for a cycle.

The following Electrochemical atomic layer deposition cycle was chosen (Figure 4.2), involving Pb deposition and its exchange for Cu. Before deposition, the EQCM electrode was cleaned according to the procedure described in the experimental section. The deposition starts with the blank being pumped in to the cell for 300s to stabilize the quartz crystal. The Au substrate was them modified with I atoms by flowing a KI solution in to the cell for 180 s at open circuit, followed by blank at open circuit for 15 s. Pb solution was then rinsed into the cell for 33 s at -0.44 V. The cell was then flushed with blank solution for 8 s at -0.44 V. After which, Cu solution was flushed through the cell for 8 s at open circuit. This was followed by another blank rinse at open circuit for 11 s.

The results of the flow cell system are shown in fig 4.3. Experiments were performed at different UPD potentials for Pb. The coverage of Pb was low for potentials positive of -0.440V. Pb coverage of 0.58ML were obtained when the Pb potential was -0.440V. Potentials negative of -0.440V corresponded to the onset of bulk deposition. For Pb layers containing bulk Pb, complete replacement of Cu did not occur. The net result was a significant Pb component in the Cu deposit.

The optimum potential of -0.440V for Pb deposition was used for Cu replacement and was studied using the EQCM, without an iodine rinse in each cycle. The ALD program used was mentioned in the previous paragraph. After 10 SLRR cycles of Cu for Pb (Figure 4.4), the charge for Pb deposition and the mass change (Δf) for Cu deposition was determined. The average charge for Pb deposition was around 0.91ML; the average copper coverage based on mass was 0.54 ML. At the end of 10 cycles, the Cu was oxidized in blank solution at +0.700V. The oxidative charge was used to calculate the average Cu coverage per cycle, which came to 0.50ML. Iodide solution was flowed for

2min at open circuit before and after oxidation of Cu in blank in order to have identical surfaces and solutions to calculate Cu coverage from the oxidative mass change, 0.51ML per cycle.

In the next experiment (Fig 4.5) with iodide rinse in each cycle was done for 10 cycles of SLRR of Pb by Cu. The average charge for Pb deposition was around 0.80ML; the average copper coverage based on mass was 0.25 ML. At the end of 10 cycles, Cu was oxidized in blank solution at +0.700V. The oxidative charge was used to calculate the average Cu coverage per cycle, which came to 0.30ML. Iodide solution was flowed for 2min at open circuit before and after Cu oxidation in blank, to have an identical surface to calculate the Cu coverage from the oxidative mass change, 0.29ML per cycle. The low coverage for Cu, when iodide was introduced each cycle was not clearly understood and more studies are needed using the flow cell system to find the optimum conditions.

Conclusion

Thin films of Cu were grown on gold Via Electrochemical (ALD) using surface limited redox replacement (SLRR) reactions. EQCM was used to calculate the coverages of copper during redox replacement in each cycle, based on the mass change. Also the Cu was oxidized at the end of the 10th cycle and the coverages were calculated based on the oxidative charge and mass change.

Pb was deposited at -0.440V and replaced by copper at open circuit. The average copper coverage, based on mass and charge, during oxidation was 0.51 ML/cycle and 0.50ML/cycle respectively, without iodine rinse in each cycle. With the iodine rinse, the average copper coverage based on mass and charge during oxidation was 0.29 ML/cycle and 0.30ML/cycle respectively.

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Figure Captions

Fig 4.1: Electrochemical atomic layer deposition (ALD) cycle for SLRR of Pb by Cu without iodine rinse in each cycle.

Fig 4.2: Average Pb coverage at various deposition potentials.

Fig 4.3: Ten cycles redox replacement of Pb by Cu without iodine in each cycle.

Fig 4.4: Pb coverage (charge) and Cu coverage (mass change) for ten cycles of redox replacement of Pb by Cu without iodine rinse in each cycle.

Fig 4.5: Electrochemical atomic layer deposition (ALD) cycle for SLRR of Pb by Cu with iodine rinse in each cycle.

Fig 4.6: Ten cycles redox replacement of Pb by Cu with iodine rinse in each cycle.

Fig 4.7: Pb coverage (charge) and Cu coverage (mass change) for ten cycles of redox replacement of Pb by Cu with iodine rinse in each cycle.

Fig 4.1

Program used:

Initial Blank	300s	(Open Circuit)	
Iodine Flow	180s	(Open Circuit)	
Blank Rinse	15s	OCP	
Flow Pb	33s	-0.440V	10 Cycles
Flow Blank	8s	-0.440V	
Flow Cu	8s	Open Circuit	
Flow Blank	11s	Open Circuit	
Flow Iodine	120s	Open Circuit	
Flow Blank	20s	0.700V	
Flow Iodine	120s	Open Circuit	
Flow Blank	15s	Open Circuit	

Fig 4.2

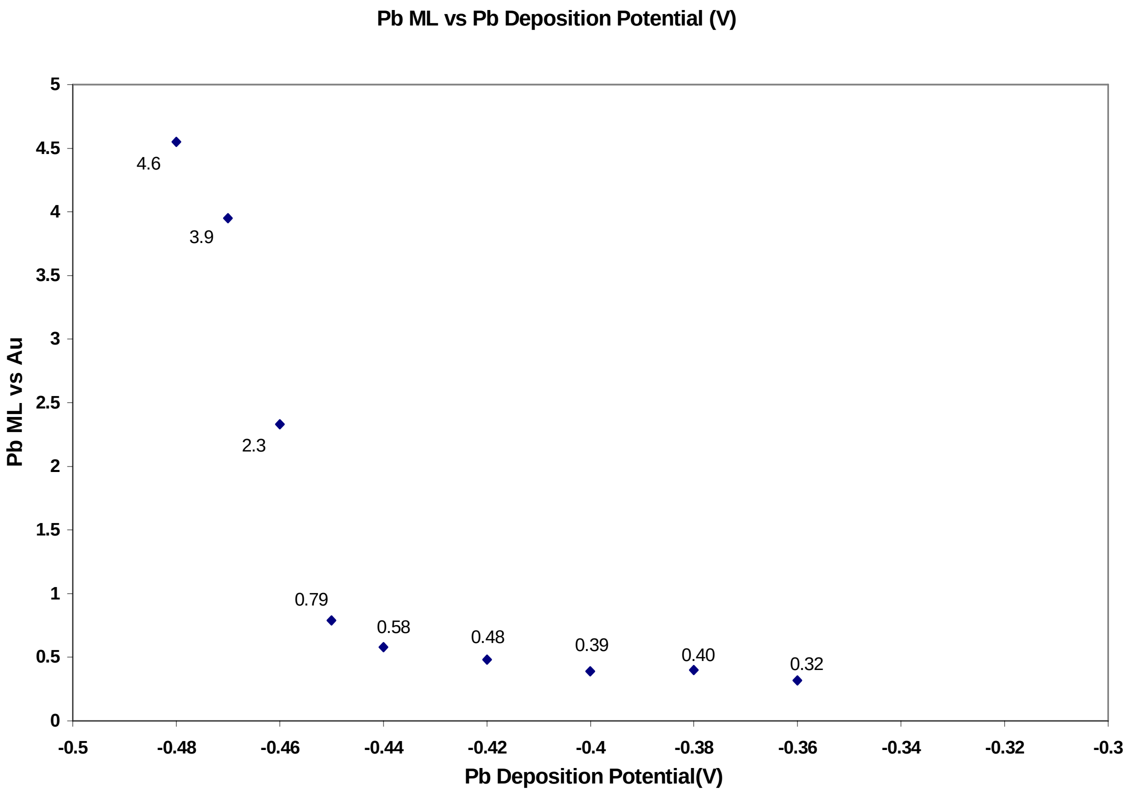

Pb ML vs Pb Deposition Potential (V)
Pb ML vs Au
Pb Deposition Potential(V)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
-0.48
-0.46
-0.44
-0.42
-0.4
-0.38
-0.36
-0.34
-0.32
-0.3
4.6
3.9
2.3
0.79
0.58
0.48
0.39
0.40
0.32

Fig 4.3

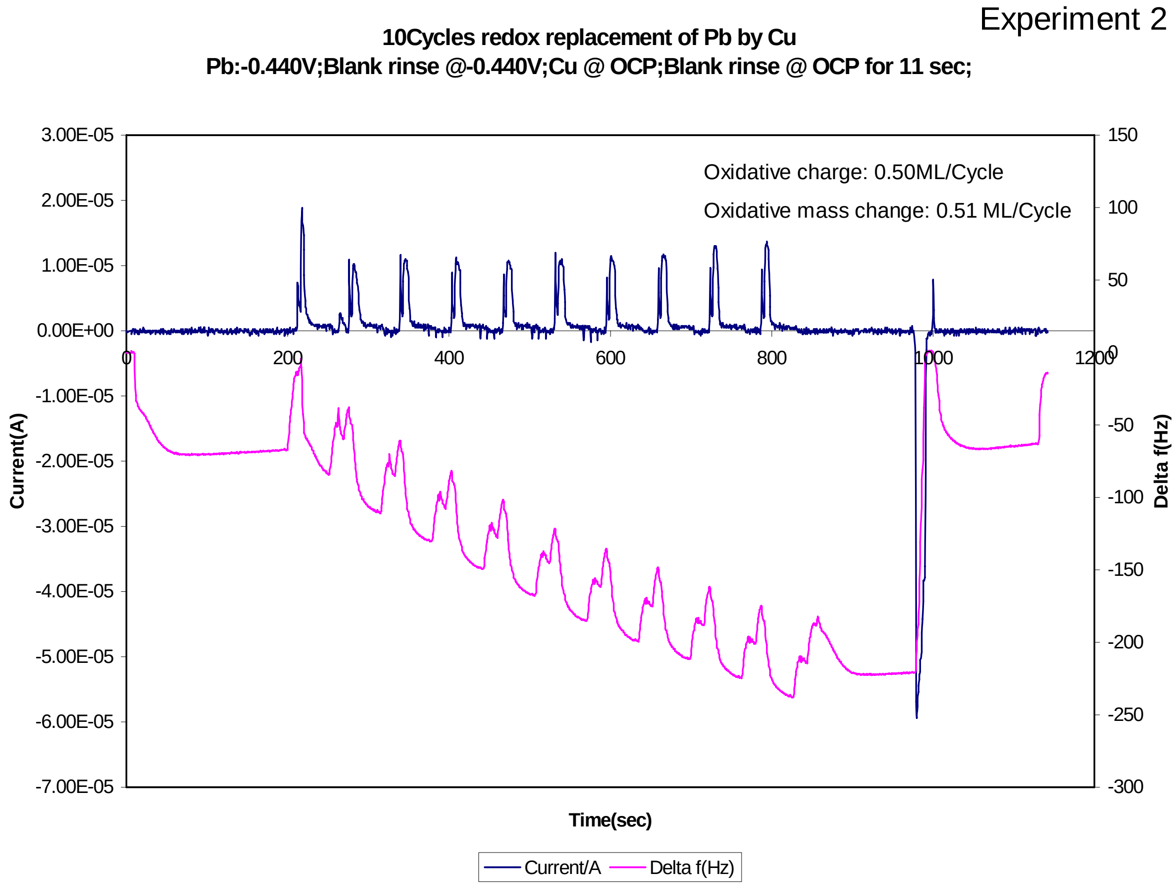

Experiment 2
10Cycles redox replacement of Pb by Cu
Pb:-0.440V;Blank rinse @-0.440V;Cu @ OCP;Blank rinse @ OCP for 11 sec;
Oxidative charge: 0.50ML/Cycle
Oxidative mass change: 0.51 ML/Cycle
3.00E-05
2.00E-05
1.00E-05
0.00E+00
-1.00E-05
-2.00E-05
-3.00E-05
-4.00E-05
-5.00E-05
-6.00E-05
-7.00E-05
Current(A)
0
200
400
600
800
1000
1200
Time(sec)
150
100
50
0
-50
-100
-150
-200
-250
-300
Delta f(Hz)
Current/A
Delta f(Hz)

Fig 4.4

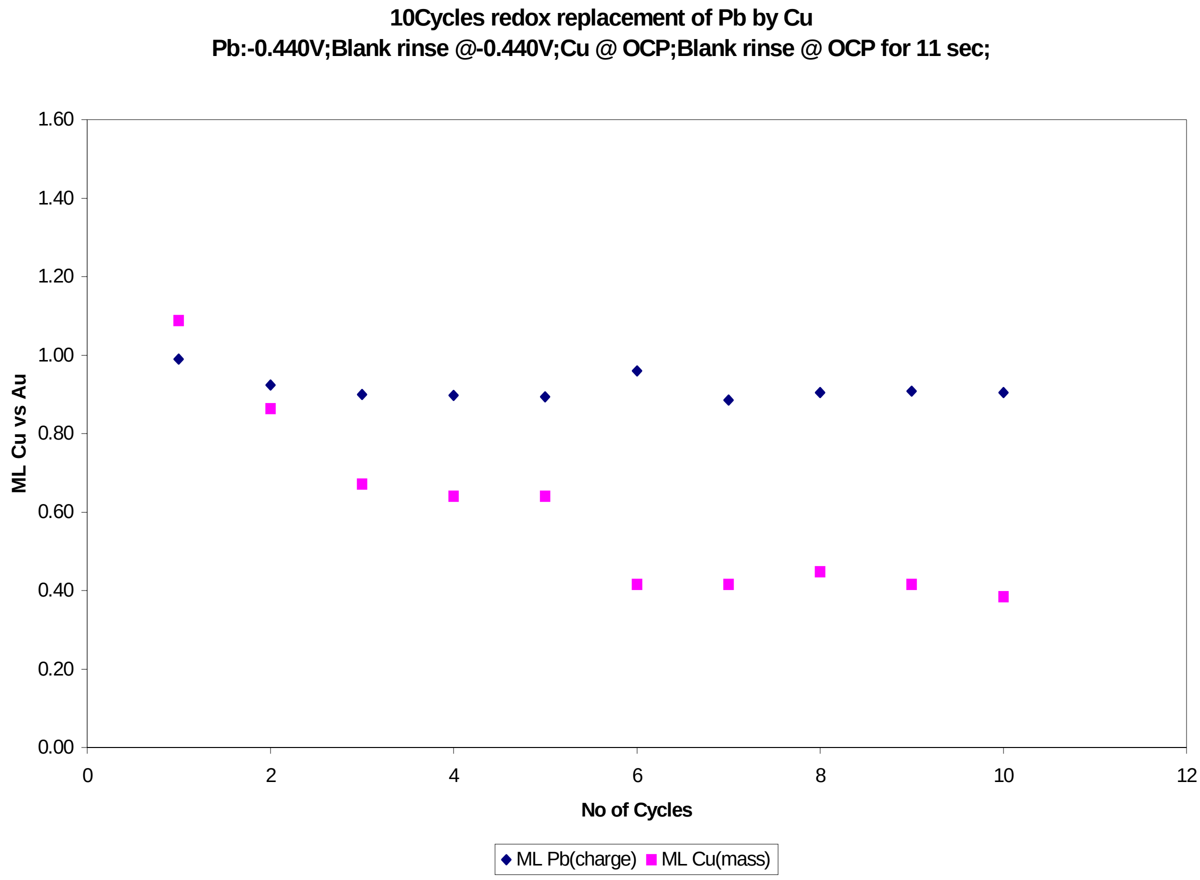

10Cycles redox replacement of Pb by Cu
Pb:-0.440V;Blank rinse @-0.440V;Cu @ OCP;Blank rinse @ OCP for 11 sec;
ML Cu vs Au
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0
2
4
6
8
10
12
No of Cycles
◆ ML Pb(charge)
■ ML Cu(mass)

Fig 4.5

Program used:

Initial Blank	300s	(Open Circuit)	
Iodine Flow	180s	(Open Circuit)	
Blank Rinse	15s	OCP	
Flow Pb	33s	-0.440V	10 Cycles
Flow Blank	8s	-0.440V	
Flow Cu	8s	Open Circuit	
Flow Blank	8s	Open Circuit	
Iodine flow	8s	Open Circuit	
Blank Rinse	8s	Open Circuit	
Flow Iodine	120s	Open Circuit	
Flow Blank	20s	0.700V	
Flow Iodine	120s	Open Circuit	
Flow Blank	15s	Open Circuit	

Fig 4.6

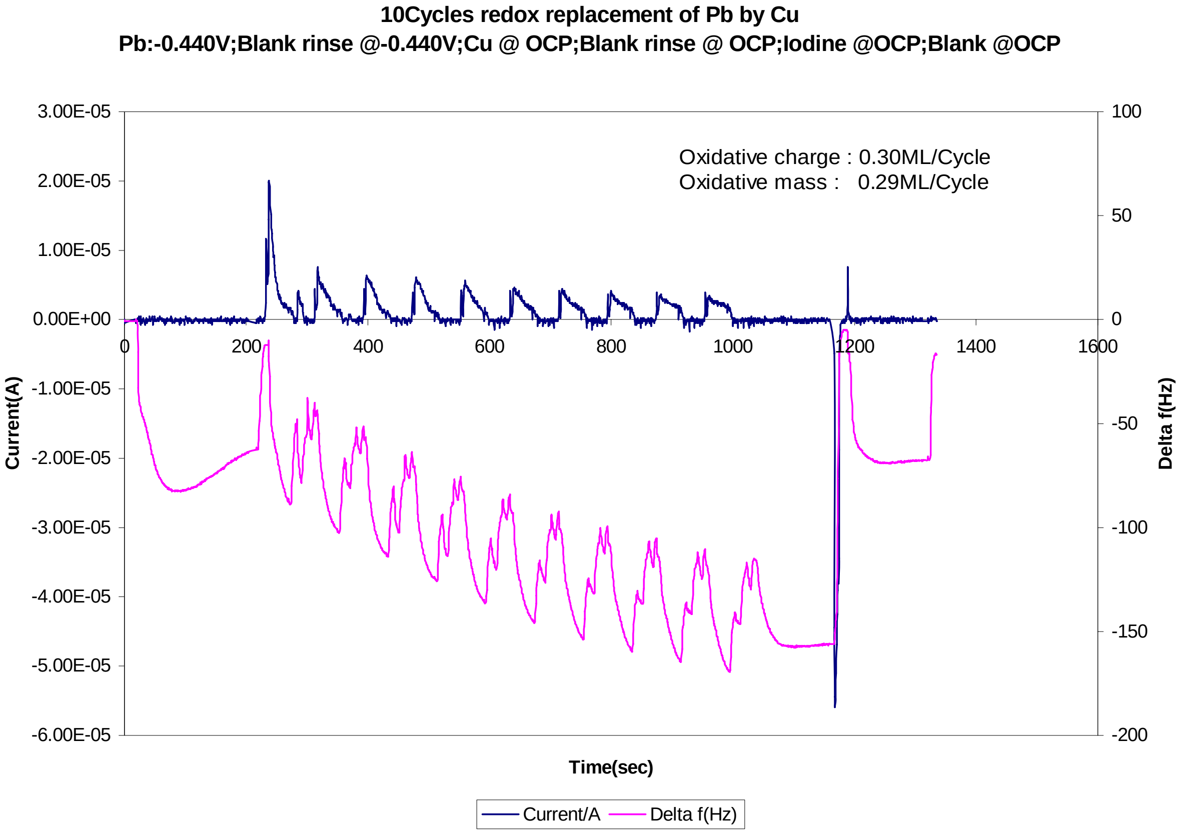
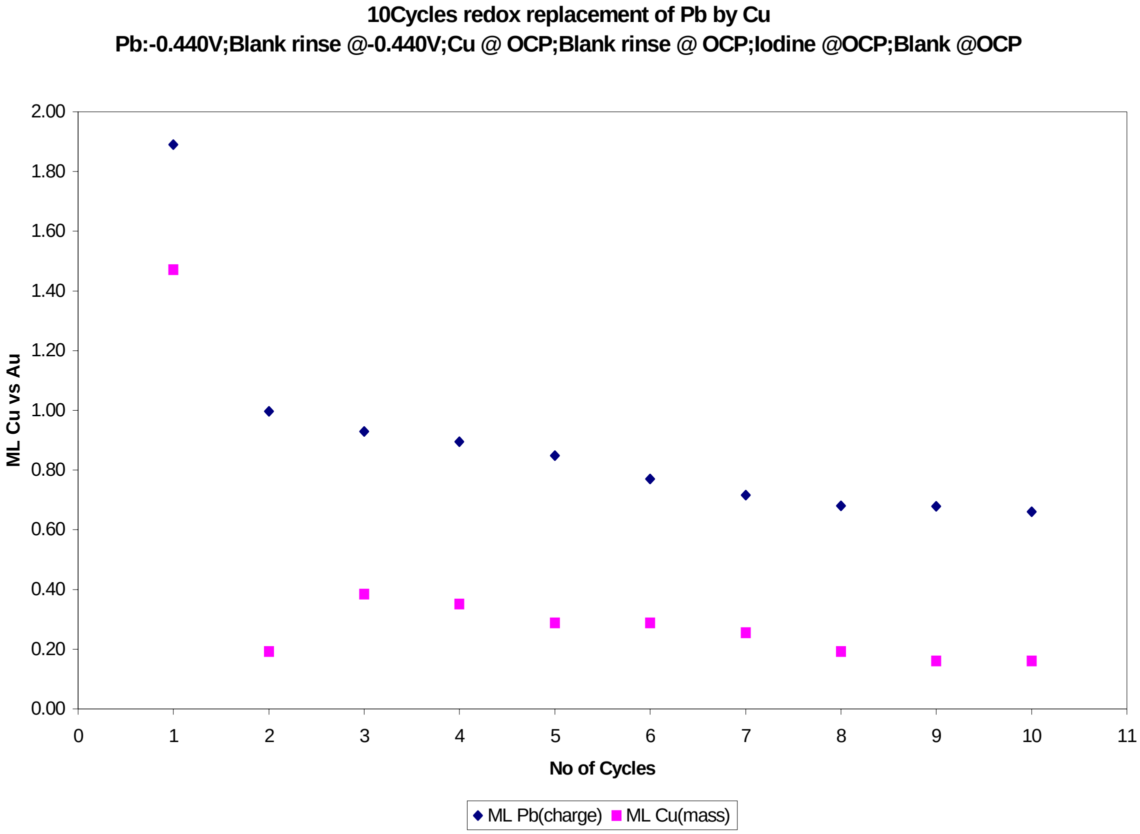

10Cycles redox replacement of Pb by Cu
Pb:-0.440V;Blank rinse @-0.440V;Cu @ OCP;Blank rinse @ OCP;Iodine @OCP;Blank @OCP
Oxidative charge : 0.30ML/Cycle
Oxidative mass : 0.29ML/Cycle
Current(A)
Delta f(Hz)
Time(sec)
3.00E-05
2.00E-05
1.00E-05
0.00E+00
-1.00E-05
-2.00E-05
-3.00E-05
-4.00E-05
-5.00E-05
-6.00E-05
100
50
0
-50
-100
-150
-200
0
200
400
600
800
1000
1200
1400
1600
Current/A
Delta f(Hz)

Fig 4.7


10Cycles redox replacement of Pb by Cu
Pb:-0.440V;Blank rinse @-0.440V;Cu @ OCP;Blank rinse @ OCP;Iodine @OCP;Blank @OCP
ML Cu vs Au
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0
1
2
3
4
5
6
7
8
9
10
11
No of Cycles
◆ ML Pb(charge)
■ ML Cu(mass)

CHAPTER 5

CONCLUSION AND FUTURE STUDIES

Conclusion and Future studies

Electrochemical quartz crystal microbalance (EQCM) was used for the studies of compound semiconductors (HgTe, CdTe, HgTe/CdTe) and metal thin films (Cu) via electrochemical atomic layer deposition (ALD). The flow cell used to make deposits was modified to fit the quartz crystal. The calibration of EQCM was done using Ag deposition and cyclic voltammetry to calculate the calibration constant value. The solution flow rate of 6.00ml/min was used to carry out the deposition with minimal noise level. Solution can be flowed in to the cell using He pressure or with the peristaltic pump connected to the outlet tube. Continuous flow was used during the deposition process. Shifts in Δf was observed when the flow is stopped.

Electrochemical ALD of HgTe and HgTe/CdTe was carried out in the flow cell system and the conditions were optimized. There were several questions that remained unanswered. EQCM was used to study the optimum conditions and to better understand the deposition process. EQCM was also used to monitor the mass changes during surface limited redox replacement (SLRR) of Cu for Pb at open circuit.

The electrochemical atomic layer deposition of compound semiconductors (PbSe, PbTe, Bi_2Te_3 and Sb_2Te_3) and metal thin films (Cu, Pt, Co and Ru) should be studied using EQCM.