BILLY HUGH FLOWERS JR.

The Automation of Electrochemical Atomic Layer Epitaxy (EC-ALE) for the Production of Thin Film Semiconductors (Under the direction of JOHN L. STICKNEY)

Presented here are the details of the automation of a novel yet attractive methodology of producing thin film semiconducting structures. This method, electrochemical atomic layer epitaxy, or EC-ALE, offers many advantages over conventional methods. Most important of these are the benefits to be gained in the ability to fabricate semiconducting thin films at room temperatures and pressures. Also of note is the EC-ALE process' ability to minimize waste production, both in volume and toxicity. EC-ALE is the electrochemical analog of atomic layer epitaxy (ALE). EC-ALE employs under potential deposition (UPD) to deposit atomic monolayers of a compound semiconductor's constituents in repetitive cycles. Automation of these cycles allows for their faithful repetition, up to 1500 times or more. The number of cycles deposited in an experiment determines the thickness of the EC-ALE electrodeposit.

The evolution and development of the automation hardware is discussed in depth. The efficacy of the hardware has been evaluated by forming EC-ALE deposits of both CdTe and CdSe semiconductors. These deposits were analyzed by electron microprobe spectroscopy (EPMA), grazing angle X-ray diffraction (XRD), scanning infrared absorption, and optical microscopy as feedback, both to improve upon the implementation of EC-ALE and as a barometer of various hardware configurations.

INDEX WORDS: Electrochemical atomic layer epitaxy, EC-ALE, ECALE, electrodeposition, atomic layer epitaxy, ALE, thin films, underpotential deposition, UPD, thin layer flow cell, electrochemical flow cell, compound semiconductor, electron probe microanalysis, EPMA, X-ray diffraction, XRD, infrared absorption, automation, semiconducting thin films, room temperature deposition, cadmium telluride, CdTe, cadmium selenide, CdSe, cadmium, Cd, tellurium, Te, selenium, Se, electrochemistry, waste minimization, waste control, heat induced interdiffussion, interface, band gap, exchange current, surface diffusion, deposition rate, codeposition, molecular beam epitaxy, MBE, vapor phase epitaxy, VPE., AFM, atomic force microscopoy, STM, scanning tunneling microscopy

THE AUTOMATION OF ELECTROCHEMICAL ATOMIC LAYER EPITAXY (EC-ALE) FOR THE PRODUCTION OF THIN FILM SEMICONDUCTORS

by

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DEDICATION

To my parents, Billy and Shelby, who instilled in me very early that an education is the most valuable asset one can hold. Their efforts afforded me with an excellent primary education and their confidence prompted me to return to school and complete my higher education. To both my ex-wives: had they not exercised the foresight to separate themselves from me, I would never have returned to college. To my son, Christopher: this should be an example to you that you are never too old, and that every cloud has a silver lining. Take note, son, that few situations are either all good or all bad-most lie somewhere in between.

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

The cutting edge of materials science is now centered on controlling the formation of structures on the nanometer scale. For compound semiconductors this idea is collectively known as bandgap engineering, essentially tailoring the behavior of semiconductors to suit whatever needs are envisioned for their implementation. The electronic structure, or bandgap, of a semiconductor can be adjusted over a wide range, through strict control of the dimensions within that structure. This is analogous to the "particle in a box" quantum mechanical model. Essentially, confining an electron, or putting it into a smaller box, is manifested in a wider separation of energy levels. Bandgap engineering is undifferentiated from the quantum model, as modifying either the size of the particles or the thickness of the layers that comprise a thin film semiconductor subsequently alters its electronic properties. More specifically, smaller dimensions mean larger bandgaps.

Thin films of II-VI compounds enjoy a wide and ever growing range of applications, such as solid state lasers [9], luminescent displays [1-3], radiation detectors [1-4], high power laser windows [4,7], infrared detectors [4-6], photovoltaics [1,2], and photoelectrochemical solar cells [8]. The efficiencies and longevity of such devices is directly linked to the quality of these structures at the atomic level. Lack of contamination, coherent crystal structure, and crystal size are the primary considerations in producing quality structures. In the realm of compound semiconductors, interface quality must be considered as well. Crisp, well-defined interfaces, on an atomic scale, are essential if the goal of viable devices is to be realized. As the applications of compound semiconductors expand, so does their complexity. This need to produce structures having more intricate layering schemes, possibly having layers of varying

thicknesses, only exacerbates the tasks of both generating and maintaining quality interfaces. Superlattices, or structures composed of two, three, or even four semiconducting compounds, arranged in repeating units, are excellent examples of how the edge of the envelope work in this field mandates a growth methodology that can exercise the kind of control discussed above [10].

Conventional directions in this endeavor are usually molecular beam epitaxy (MBE) [16-21], vapor phase epitaxy (VPE) [22-24], or various permutations of vacuum related techniques [25]. None of these methods can address the consideration of maintaining the crisp interfaces discussed above, as all suffer from the specter of heatinduced interdiffussion of component species. Even temperatures of 200-500 °C, relatively low for MBE or VPE, are deleterious in this respect, and many species desirable for incorporation into semiconducting structures are more labile than others. These methods are also somewhat inimical both to research budgets and to the environment, as they require expensive equipment, the use of costly and ultra pure precursors, and produce large volumes of highly toxic, often gas phase, wastes. Additionally, these methodologies cannot neglect the often-encountered disparities in thermal expansion coefficients amongst constituent species. Even if a high quality structure is produced at elevated temperatures, cooling to ambient conditions will inevitably lead to stresses, cracking, and device failure as constituents cool at varying rates.

The work detailed in this volume is concerned with an alternate modus of producing thin film compound semiconductors known as EC-ALE, or electrochemical atomic layer epitaxy. Electrodeposition is a century old technique for plating metallic thin films that has been steadily finding increased favor in the production of semiconducting thin films [see reviews, 11-15]. More important, however, is the work pioneered by IBM [26] in 1998 with regard to the dual damascene [26,27] copper plating technique. This method currently defines the front lines in the struggle of fabricating high quality copper interconnects for ultra large-scale integration chips on silicon. One does not have to search far for indications of the viability of this technique, as virtually all of the well known chip producers, namely International Business Machines, Motorola, American Microchip Devices, Intel, and others have incorporated silicon wafer electroplating machines into their production lines.

At this point a definition of *epitaxy* is in order. The conventional idea of epitaxy revolves around single crystal work, where a single crystal is used as a template, or substrate, to accept ad layers of the same compound, having the same lattice parameters as the substrate. Compared to the goal of forming heterojunctions, or an interface between two different species or elements, as is the case of EC-ALE, homoepitaxy is elementary. Once one has chosen useable substrates and the proper compounds to construct a semiconductor, heterojunctions must exist in the scheme, and lattice constants of constituents rarely coincide. This means that as a semiconductor is fabricated, lattice strain inevitably develops. At some point, relaxation mechanisms, all of which introduce efficiency sapping defects, will exert themselves to relieve this strain. In a conventional sense, epitaxy is strictly defined as a 1 to 1 ratio between substrate atoms and ad atoms. This description does not transfer well to the idea of epitaxial semiconductor deposits, a result of lattice mismatch already mentioned. In the parlance of compound

or a compound, one single atomic layer at a time, with no 3-D growth. This twodimensional growth scheme leads directly to the crisp interfaces mentioned earlier.

The latter half of the 20^{th} century has seen a sizable investment in the idea of epitaxy in electrodeposition [26-29]. The principles involved are analogous to MBE and VPE, in that an intricate interplay between deposition rates and surface diffusion is the key. The goal of this is ALE, or atomic layer epitaxy, a route originally explored as a means of improving MBE and VPE fabricated structures by minimizing 3-D growth. Atoms on the surface must be allowed to diffuse to optimal sites. But, if the deposition rate is too fast, ad atoms' ability to accomplish this is curtailed. Generally, epitaxy is tractable only if the rate of surface diffusion outstrips that of the deposition rate. This is the key to the established success of MBE and VPE. Both methods employ elevated temperatures of substrates and/or impinging atoms to enhance surface diffusion. But the darker side of these high temperature methods has been previously established. The keystone of EC-ALE is the production of compound thin film semiconductors, from solution, under ambient conditions. Simply utilizing low volume deposition cells circumvents the need for vacuum. Vacuum systems operate in the molecular flow regime to control contaminants, while EC-ALE simply limits the concentration of contaminants available to the substrate by virtue of reduced solution volumes. But biasing the deposition rate/surface diffusion coactions without the aid of added thermal energy is a different matter. EC-ALE utilizes a well-known process, underpotential deposition, or UPD, [30-35] to address this issue.

The UPD process is no stranger to electrochemists [31,34,36-38]. Its simplest explanation is that its driving force is an energy minimum, a result of the Gibbs free

energy of formation of compounds. In practice, the deposition of a single atomic monolayer of a species onto a dissimilar substrate is more facile than the formation of a bulk structure. This means that an atomic monolayer is accessible with less energy input than bulk, or 3-D, deposition. For electrochemists, this allows single atomic monolayers to be deposited at potentials positive of, or less reductive than, those required for bulk deposition. When the UPD layer forms, the resulting structure becomes in essence an alloy, affecting the shift in the Gibbs free energy. In addition, UPD is surface-limited, or self-quenching. Once the surface is covered with the initial UPD atomic monolayer, there is no incitation for further deposition. Assuming that excessively harsh conditions, or a potential approaching levels that would be needed to produce bulk deposits, are not imposed on the system, no 3-D growth occurs. It is this energy minimum that allows the EC-ALE methodology to be viable. The UPD condition lies on the cusp of the classic equilibrium, or formal potential, which is fortuitous from the standpoint of electrochemical ALE. This is the point at which electrochemical ALE must be performed, as these are the conditions under which electrodeposition is a dynamic process, and deposition rates are mitigated in by the exchange current. The need for low deposition rates in ALE has been discussed, and while surface diffusion is low at room temperature, increased exchange current supplants that process. In this dynamic regime, atoms that deposit in less than optimal sites will dissolve back into solution, seeking to find a more amenable deposition spot later, driven back to the surface by the increased exchange current. On the other hand, atoms that deposit in optimal sites are stable, by virtue of the UPD energy minimum. Conversely, if excessively harsh conditions are imposed, as in the production of bulk deposits, deposition rates will exceed exchange

rates, and 3-D growth will be the result [15]. EC-ALE is no more than the melding of UPD and ALE (atomic layer epitaxy) into a common construct [39-43]. Figure 1.1 illustrates how UPD can be used to produce a multi layered CdTe electrodeposit, while (Figure 1.2) elucidates electrochemical UPD in a cyclic voltammogram of Cd on Au.

EC-ALE is certainly not the only electrochemical technique employed in the formation of thin film semiconductors. These include: precipitation, codeposition, annealing techniques, pulse plating, and electrochemical ALE [13, 39, 44-50]. The precipitation methods make use of electrochemical oxidation or reduction of a first element in a solution containing a soluble form of the second constituent of the compound semiconductor. The result is the spontaneous precipitation of the compound, directed towards the electrode, or nucleation center. Codeposition, the most prevalent methodology currently in use, involves the use of soluble oxidized precursors of all the elements making up the compound in a single bath. The stoichiometry of the system is maintained by selecting potentials in such a way that the less noble species (more reactive), or the first to be deposited, will not deposit on itself, but only on the second element in the scheme, or the more noble (less reactive) of the two. The concentration of the more noble partner is diminutive (ratios of 10:1 are normal) relative to the less noble member. In this way, the second element quickly reacts to form the compound as the higher concentration first element arrives at the surface, and 3-D growth is avoided. Pulse plating uses a fast cycling potential program and reductive UPD to control growth.

Figure 1.1: Cartoon of the EC-ALE process. A clean Au substrate is seen in 1.1a. Cd ad atoms are electrodeposited from solution, using UPD potentials, in 1.1b. In 1.1c, the UPD electrodeposition of Te has formed one complete monolayer of the semiconductor CdTe. This represents one EC-ALE cycle, and automation of the methodology allows this cycle to be repeated as many times as needed. This determines the thickness of the EC-ALE deposit.







Figure 1.2: Cyclic voltammogram of 5.0 mM CdSO₄ solution in 0.50M Na₂SO₄ matrix, pH 5.7.



The annealing techniques (also known as two stage methods) have produced photovoltaics with efficiencies as high as 17.7% [51]. This approach can easily control stoichiometry, but the drawbacks of using high (annealing) temperatures have been discussed.

The methodology of EC-ALE affords it many inherent advantages. The benefits of operating at ambient temperatures and pressures have been discussed. As far as MBE and VPE are concerned, EC-ALE's prospects of using solution phase precursors and producing liquid wastes containing only millimolar concentrations of toxins are quite attractive. In reference to all other methods, EC-ALE affords the researcher with increased opportunities to investigate the finer points of electrochemical ALE. This is because EC-ALE involves many separate steps. Each step can be considered a control point, or variable, each of which can be studied separately. These include, but are not limited to, solution pH, the concentrations of deposition species, solution flow rates, complexing agents, electrolytes, imposed potentials, and a myriad of hardware considerations. The solution variables are in turn multiplied by the fact that normally several distinct solutions, such as a deposition solution and a rinsing blank for each constituent, are often used. While the scope of this variable space is intimidating, working in this area is well worth the effort, as it follows that each variable can also be individually optimized. This will inevitably lead to higher quality devices. Finally, the prospects of accessing new materials must be considered, as the technique is orthogonal to the more conventional approaches of MBE and VPE [15].

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CHAPTER 2

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THE EVOLUTION AND DEVELOPMENT OF THE AUTOMATED EC-ALE HARDWARE

The story of EC-ALE would be seriously lacking without a discussion of the development of the hardware used and some elucidation of the thinking that provided the impetus for various hardware changes. The equipment used has seen innumerable permutations. The original efforts at producing thin film semiconductors by EC-ALE in the Stickney group investigated the feasibility of the process using the TLE, or thin layer electrode [1]. The TLE is of special importance to EC-ALE, as it serves as the primary tool for determining the feasibility of producing thin films from constituent species, deciding which solution schemes are the best (along with Pourbaix diagrams) [2], and what potentials might be prudent in the effort. Advantages of the TLE in this work are centered around very low solution volumes, on the order of 5 μ l. This limits the signal response of any background reactions, which can obscure the relatively small currents associated with UPD. The concentration of contaminants in the cell is limited, and bulk deposition is curtailed by limiting the number of ions of interest available to the substrate. Also, the TLE has a well-defined electrode surface area (ca. 1.25 cm^2), facilitating accurate coulometry, while quick solution exchange allows for easy removal of any soluble species and the for the alternation of solutions, as would be the case in actually fabricating a compound semiconductor. It mimics more closely the conditions present in the EC-ALE modus, namely ambient temperatures and pressures and the use of polycrystalline Au substrates. Figure 2.1 shows a TLE. A solid base of preliminary studies is also established, using ultra high vacuum electrochemical (UHV-EC) techniques to deposit on single crystal Au surfaces. This information affords great insight into the UPD process in its initial stages, using analysis techniques such as LEED (low-energy electron diffraction) to ascertain the unit cell of ad layers and AES (Auger

Figure 2.1: A TLE, or thin layer electrode.



electron spectroscopy) to qualitatively determine surface composition [3-6]. Knowledge of surface coverage is also a necessary precursor to actual deposit formation, so STM (scanning electron microscopy) studies are done as well [4].

The first EC-ALE work in the Stickney group was indeed undertaken with the TLE, but it was immediately apparent that the tedium of faithfully reproducing solution and potential switches for a deposit greater than 10-12 layers thick made the manual method intractable. The hardware quickly evolved to utilize separate pumps for each solution, a rotary selection valve, an in-house constructed potentiostat, and a newly designed thin layer flow cell, all of which was integrated with and controlled by computer [7,8]. Not only did this system allow the repetitive, cyclic nature of EC-ALE to be explored at length (as many as 1000 cycles), but also the thin layer flow cell allowed the evaluation of different substrates and never relinquished potential control. Figure 2.2a illustrates this system, while (Figure 2.2b) shows the flow cell in detail... The initial flow cell design was not without problems. Most notable of these were excessive uncompensated cell resistance (IR drop), due to the placement of the reference electrode in the solution outflow, and the shape of the deposition area. The aspect ratio (length to width) of the deposition area was very high, resulting in a problem with "edge effects". While the flow profile was predominantly laminar, areas of poor solution exchange, mostly proximal to the long edges of the deposit area, still existed. Deposition was quite irreproducible in these areas, and with the shape of the deposit being essentially a very narrow and long rectangle; these edge effects impacted the bulk of the deposit. Additionally, the cell was constructed of stainless steel, not the material of choice for corrosive salt solutions and discreet electrical connections.

Figure 2.2: A block diagram of the first automated EC-ALE system is seen in 2.2a, while 2.2b shows a close up of the thin layer flow cell.



The next evolution brought another flow cell to fruition (Figure 2.3). This cell was constructed of Plexiglas with an emphasis on solving the problem of uncompensated resistance. This arrangement used a reference compartment mounted directly above and facing the substrate, utilizing a Vicor frit to allow electrical conductivity with the inside of the cell. However, this was still not optimal, as uncompensated resistance was still an issue due to the limitations of the frit. Also, producing these cells was problematic, as machining a number of plumbing and internal electrical connections was required, all of which had to positively seal against solution flow and pressures.

Next came the modified H-cell (Figure 2.4). In an effort to address the myriad of problems associated with the thin layer flow cell designs, this thick layer arrangement was configured. This design attempted to minimize uncompensated resistance by employing a much larger, ceramic frit for increased conductivity. This was only a marginal fix a best, as the problem of electrode placement was exacerbated (compared to the design seen in Figure 2.3). But the H-cell was fraught with many other problems, on many levels. Most importantly, the design required solution filling and draining from the bottom, which meant that potential control could not be maintained throughout the entire EC-ALE cycle. It should be mentioned, however, that excellent results have been achieved with a slight modification of the H-cell, a wall jet configuration, which corrected many shortcomings [9]. Secondly the volumes of solutions used were copious, to say the least. The cell held ca. 5 mL of solution, and the bottom fill/drain meant that the deposit had to be exposed to each new solution multiple times in order to ensure that even those drops adhering to the deposit's surface were exchanged.

Figure 2.3: The second flow cell design.


Figure 2.4: The modified H-cell deposition system.



With multiple solutions incorporated in the EC-ALE cycle, a 200-cycle run easily produced 12-15 L of waste. This is not tractable in today's environment of waste minimization. Also, a problem that was not yet realized as a major key to reproducibility, the absolute necessity of oxygen exclusion, was aggravated by the design. Solutions were well sparged with N_2 in their reservoirs, but no attempt was made to exclude O_2 from the rest of the apparatus. Draining of the H-cell, in fact, sucked in a healthy dose of O_2 with every solution exchange.

But the H-cell did allow a lot of work to be done. Much was learned about the intricacies of the EC-ALE process, and much progress was made [10,11]. Once some familiarization with the H-cell and the vagaries of EC-ALE were realized, shortcomings in the peripheral hardware became more apparent. The rotary selection valve was limiting in several ways. Not only was it questionable how strictly the solution switching operations were repeated throughout a 200-cycle experiment (possibly as many as 800 to 1000 individual valve movements), the selection valve allowed some solution mixing due to internal dead volume. Mixing of EC-ALE solutions inevitably results in salt formation, and these salt grains simply ground away at the internal surfaces as the valve rotated. This did little to preserve the reproducibility or longevity of the selection valve, and in fact, these salt grains often caused the valve to loose its alignment during a run. This became a vicious circle, as misaligned ports meant increased solution mixing which led to increased salt formation, and so on. The pumps originally used were simply not robust enough for the application. While peristaltics are still the pump of choice for EC-ALE, the peristaltics originally chosen were driven by direct current, low torque motors.

These simply could not handle the loads imposed, tended to slip (being constructed with plastic gears), and overheated.

The final evolution of the EC-ALE hardware brings this discussion up to date with what is being currently used in the Stickney lab. To address the issues mentioned directly above, larger, direct drive, higher torque, alternating current peristaltic pumps were chosen. A new selection valve, essentially 4 solenoid-actuated 3-way valves, machined into a single Teflon block, was purchased. Single solenoid valves were tried, but these had to be plumbed together, and the tubing "trees" that resulted increased dead volume to an unacceptable level. The new valve is much smaller than the rotary selection valve, and has only one internal moving part (a Teflon flap) exposed to solution. While the dead volume is not zero, it is marketed as a quick-flush valve, and the dead volume is estimated to be no more than 12 μ l. Having 4 separate valves allows 5 solutions to be employed, with no worry about the switching commands being faithfully executed, regardless of the number of commands imposed.

The single most important piece of hardware to evolve for EC-ALE is without a doubt the deposition cell that is currently in use. This development of this new flow cell resulted from a desire to return to a thin layer (more laminar) design while eliminating oxygen. The current deposition cell is seen in (Figure 2.5). The internal volume of this cell is ca. 300µl, depending on the gasket thickness, allowing a 200-cycle EC-ALE experiment to produce only ca. 1.5 L of waste. More important is the placement of both the auxiliary and reference electrodes. The new design puts the working and Figure 2.5: The current thin layer flow cell for EC-ALE.



reference electrodes face to face, separated by a gap on the order of 0.5 mm, depending on gasket thickness. This arrangement surpasses any past designs as far as uniformity of current distribution in the cell.

While the reference is still found on the solution outflow channel, it is now fitted into a relatively large cavity, yet remains very close to the deposition compartment, all without adversely impacting the rest of the cell design. This, along with the use of a smaller, more robust reference electrode (as used in chromatographic applications) minimizes uncompensated resistance. Lastly, this design promotes laminar flow in the cell to minimize areas where solution exchange is hindered.

The new pumps, solution switching valves, and deposition cell were integrated into a Plexiglas enclosure that allowed vigorous N₂ purging. The solution delivery tubes are encased in a larger, surrounding tube. This outer tube is then purged with N₂, allowing O₂ to be removed from the tubing runs as well, addressing the issue of tubing oxygen permeability. With the smaller, newer solution selection valve also inside the Plexiglas box, the system became quite amenable to O₂ exclusion. When in use, the atmosphere inside the box is monitored with an O₂ meter to ensure that O₂ levels are < 30 ppm. The current EC-ALE hardware is seen in (Figure 2.6) [12].

Some mention must also be made of the issue of substrates for EC-ALE. The decision to deposit on Au was settled on long ago. Its robust and inert nature, combined with it being readily available and the fact that its electrochemistry is well understood, made it a sapient choice. Original attempts at electrodeposition in the Stickney group were performed on commercial Au on silicon wafers. It was thought that since Si wafers

Figure 2.6: The current EC-ALE hardware. Pumps and switching valves are computer controlled, as are applied potentials via a potentiostat. Nitrogen purging of the entire solution stream, from reservoirs to the deposition cell, insures oxygen exclusion.



were the accepted substrate in the semiconductor industry, that tack would be prudent. It was also felt that high quality Si wafers could be obtained from a number of vendors, allowing some bargain hunting. In truth, the development of the EC-ALE methodology was severely limited for quite some time by these commercial substrates. Figure 2.7a is an AFM (atomic force microscopy) image of a representative of Au on Si wafer, showing the surface covered by 40 nm bumps. One could not reasonably expect to deposit anything epitaxially on such a surface, regardless of the method employed. The answer to this problem was an in-house constructed vapor deposition system, allowing the Stickney group to produce its own substrates. It was decided to start with a simple glass microscope slide, followed by evaporating a Ti cladding layer onto it, then topping it off with vapor deposited Au. These substrates could then be annealed in a H₂ flame (not possible with Si substrates) to improve crystallinity. Figure 2.7b shows an example of these substrates. These in-house produced substrates are now the main substrates used for EC-ALE.

Figure 2.7: 2.7a is an AFM image of a commercial Au on Si substrate that is wholly unsuitable for EC-ALE due to the presence of 40 nm. bumps on the surface that preclude epitaxial deposition. 2.7b is an AFM image of an annealed, in-house produced Au on glass substrate. Note the different height ("z") scales in the images. The atomically flat planes seen in 2.7b are amenable to the EC-ALE modus.





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CHAPTER 3

ATOMIC LAYER EPITAXY OF CDTE USING AN AUTOMATED ELECTROCHEMICAL THIN LAYER FLOW DEPOSITION REACTOR.¹

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ABSTRACT

CdTe deposits formed by electrochemical atomic layer epitaxy (EC-ALE), using new cycle chemistry and an automated flow cell electrodeposition system, are described. Previous studies of electrochemical (ALE) have involved atomic layer formation using reductive underpotential deposition (UPD) of one element (Cd), followed by oxidative UPD of a second element (Te, from an acidic (pH 2.0) solution) to form the EC-ALE cycle. In the present study, both basic (pH 10.2) and acidic tellurium solutions are used, allowing either the reductive or oxidative formation of Te atomic layers. Consequently, one new cycle consists of the reductive deposition of both elements, simplifying and speeding up the cycle. The irreversibility of Te atomic layer formation in the basic solution also serves to expand potential range over which the deposition is surface limited, from 0.10 V using the previous cycle, to 0.6 V utilizing the present chemistry. Finally, the new cycle chemistry allowed the amount of deposit formed each cycle to increase from 0.4 monolayers (ML) per cycle to 1 ML per cycle in the present study. The new hardware involves use of a thin layer flow cell with a 1X3 cm deposition area. In the previous deposition cell, the substrate was suspended in one side of an electrochemical H-cell, and simply draining and refilling the cell exchanged solutions. Two major problems with this configuration were the large volumes of solution used with each filling of the cell, about 5 mL, and that potential control of the deposit was lost each time the solution was drained through the bottom fill/drain arrangement. This free ranging potential can be quite deleterious. Other changes have included the encasement of the pumps in a Plexiglas cabinet and the sheathing of solution delivery tubes to lower

the amount of oxygen in the deposition environment. Prior to deposition experiments, the environment inside the box is purged to < 30 ppm O₂.

INTRODUCTION

Other than oxides, CdTe is the most extensively electrodeposited compound semiconductor [1-10]. Energy conversion has been the impetus for most studies of CdTe electrodeposition, directed towards the formation of photovoltaics. High quality CdTe based photovoltaics are commercially produced using electrodeposition.

The advantages of electrodeposition include the fact that most compound semiconductor electrodeposition is performed at or near room temperature, which is considered low temperature formation for these materials. Low temperature deposition is desirable for avoiding heat-induced interdiffussion of adjacent layers of a structure. Electrodeposition also promotes conformal growth on other than flat surfaces, and it is generally a low cost methodology. The most important reason for pursuing electrodeposition as a thin film formation methodology is that it is orthogonal to MBE and CVD methods, suggesting that some compounds and structures might be formed electrochemically that are not accessible by the more conventional methods.

Electrodeposition methodologies for compound deposition are well reviewed in the literature, and include techniques referred to here as: Precipitation, Codeposition, Two Stage, and Electrochemical ALE [1-9]. The precipitation methods involve electrochemical oxidation (or reduction) of a first element in a solution containing a soluble form of a second, complementary, element, so the compound precipitates. A good example would be oxidation of Cd to Cd^{2+} in a solution that contains S^{2-} ions. The electrode can act as a nucleation center for the precipitation of CdS, as the Cd^{2+} is generated at the electrode surface. The growth mechanism is closely related to oxide formation on reactive metals.

Codeposition involves the use of soluble oxidized precursors of all the elements making up the compound in a single bath. A good example is when Cd²⁺ and HTeO₂⁺ are simultaneously reduced to form a deposit. Stoichiometry is maintained by using a potential where the first (less noble) element (Cd) only deposits on the second (more noble) element (Te), and not on itself. This is referred to as underpotential deposition (UPD) [10-14]. The concentration of the second element is kept low, so that as it deposits, it is rapidly converted to the compound by deposition of the more numerous first element. Codeposition is the most widely used compound electrodeposition methodology at present.

The designation "Two Stage" encompasses a large variety of methods. Common to all is the initial formation of precursor films of constituent elements or alloys, where at least one of the layers has been electrodeposited. The resulting film is then annealed (some times in a gas containing one of the constituent elements) to form the compound. This methodology is proving to be quite useful for the formation of chalcopyrite compounds such as CuInSe₂[15-30]. Some of these compounds have been used to form photovoltaics with efficiencies as high as 17.7% [31].

Electrochemical ALE (EC-ALE) refers to the electrochemical analog of atomic layer epitaxy (ALE). The principle of ALE is that a deposit is formed one atomic layer at a time, using surface limited reactions, in a cycle [32-36]. Using these 2-D (surface limited) reactions, 3-D growth is minimized and epitaxy is promoted. In electrochemistry, surface limited depositions are generally referred to as underpotential deposits (UPD) [10, 12; 37, 38]. The potential needed to form a first atomic layer of one element on a second frequently occurs at a potential prior to (under) that needed to deposit the element on itself. The first atomic layer forms because of the favorable free energy of formation of a surface compound. Use of UPD for ALE is referred to here as electrochemical ALE. Separate solutions and potentials are used to electrochemically deposit atomic layers of each element in a cycle. Ideally, one cycle of deposition results in the formation of one compound monolayer, and the number of cycles determines the overall thickness of the complete electrodeposit.

In order to grow deposits of more than about 10 cycles, the deposition should be automated. Several instruments have been built to form deposits using electrochemical ALE [39-43]. The first report used a small thin layer flow cell, much like those used in electrochemical detectors for liquid chromatography [39]. There were considerable problems with irreproducibility, bubbles and edge effects in those studies, making the results difficult to interpret. The design, however, was relatively simple and used very small volumes of solution.

A simple H-cell configuration, where solutions were pumped in and drained out through the bottom, was then tried. The reproducibility was far greater than the previous thin layer flow cell system, greatly improving the homogeneity of the deposits. Thin films of CdTe, CdSe, and CdS were formed using the H-cell system [41], and a more detailed study of CdTe deposition as a function of a number of cycle variables was pursued [40]. Variables studied included: Cd and Te deposition potentials, coverage as a function of the number of cycles, rinsing conditions and substrate dependence. Those results suggested that the best quality 200-cycle thick deposits were visually blue in color. CdTe is a direct band gap semiconductor, absorbing strongly in the visible region of the electromagnetic spectrum. This makes it easy to ascertain roughly how thick the deposits are by visual inspection, the color of a deposit being a function of interference effects within the thin film.

The use of inductively coupled plasma-mass spectrometry (ICP-MS) on dissolved samples, however, indicated that the blue deposits were thinner than anticipated, 85 monolayers (ML) thick, instead of the 200 ML expected. This suggested that the optimized cycle was producing only 0.4 ML per cycle. Similar conclusions were subsequently drawn from ellipsometric studies of the deposits.

Villegas et al. developed an automated wall jet deposition system for CdTe EC-ALE [42]. The high quality of their deposits was demonstrated with transmission electron micrographs (TEM), which clearly show the epitaxial nature of the deposits. Foresti et al. have developed an automated flow cell system using a cylindrical cavity, with the substrate covering one end of the cylinder and the auxiliary electrode covering the other. Their system has been used to deposit CdS and ZnS using EC-ALE [43].

A similar automated instrument was used by Nicolau et al. [44] to form deposits by sequential ionic layer adsorption reaction (SILAR), which amounts to chemical bath ALE. Rajeshwar et al used an electrochemical flow cell deposition system to form CdSe and ZnSe [45]. In their studies, thin films of each compound were formed using codeposition, not EC-ALE, and the flow cell was used to alternate the deposition of each film to create a superlattice. The present article describes important changes to the deposition cycle and flow cell hardware. These changes have resulted in significantly increased deposition rates, better control over the deposits, more reproducibility, and near optimization of the coverage per cycle.

EXPERIMENTAL

The basic flow deposition system is schematically diagramed in (Figure 3.1), and consists of a PC computer with an Advantec 812 board controlling peristaltic pumps (Cole Parmer) and a solenoid driven, 4-way, Teflon distribution valve (NResearch). The potentiostat was built in-house, using simple op-amp circuits. The pumps, valves and potentiostat are similar to those described by this group in previous reports [39-40, 41].

Initial studies with an automated flow deposition system for EC-ALE used a small thin layer flow cell [41], producing deposits that were only 1X10 mm² (Figure 3.2). Again, reproducibility was a major problem, as deposits were greatly affected by bubbles trapped over the deposit and flow effects near the gasket edges, exacerbated by the small physical size of the deposit. As noted above, the thin layer flow cell was then replaced with a modified electrochemical H-cell (Figure 3.3), where larger, 1X3 cm² substrates were simply hung in one side of the Pyrex H-cell, having a capacity of several mL of solution. There were then no bubble problems or gasket edge problems [39, 40], and good quality, homogeneous deposits were formed. Problems with the H-cell were that several mL of solution were used for each rinse as opposed to the 10 μ L used with the thin layer flow cell [41]. Perhaps most disturbing was that potential control was lost with each rinse as the solution was drained. It was also determined that oxygen needed to be

Figure 3.1: The current EC-ALE hardware. Pumps and switching valves are computer controlled, as are applied potentials via a potentiostat. Nitrogen purging of the entire solution stream, from reservoirs to the deposition cell, insures oxygen exclusion.



Figure 3.2: A block diagram of the first automated EC-ALE system is seen in 3.2a, while 3.2b shows a close up of the thin layer flow cell.



Figure 3.3: The modified H-cell deposition system.



In the present study, the H-cell has been replaced by the flow cell shown in (Figure 3.4). In some ways the cell in (Figure 3.4) is just a larger version of the thin layer flow cell used originally (Figure 3.2) [41], where 1X3 cm² deposits are formed instead of $1X10 \text{ mm}^2$ deposits. Advantages of using the flow cell are that potential control is maintained during the whole run, and relative to the H-cell, much smaller volumes of solution are required [39, 40]. To promote a more laminar flow profile through the 1 cm wide cell, the channel was flared at the inlets and outlets (Figure 3.4). The wall of the flow cell channel opposite the substrate was made from an indium tin oxide (ITO) thin film electrode, serving as an auxiliary. The transparency of the auxiliary electrode allowed visual monitoring of bubbles and facilitated the monitoring of deposit growth. The ITO was not as robust as desired, however, and was frequently supplemented with some vapor-deposited (through a mask) Au stripes. The reference electrode was mounted in the outlet stream of the cell body to avoid problems with contamination. This placement also minimized the distance between the reference and the deposit, improving potential control. A Ag/AgCl (3 N NaCl) reference electrode (Bio Analytical Systems) was used, and all potentials are reported relative to it. This low cell volume greatly decreased the amount of solution required for each experiment. The silicone gaskets used varied from 0.2-0.6 mm in thickness, with a 0.4 mm type resulting in a cell volume of ca. 200 µL.

Figure 3.4: The current thin layer flow cell for EC-ALE.



The larger size of the deposits in this flow cell (Figure 3.4) minimized gasket edge effects, and careful degassing and optimization of the plumbing limited the number of bubbles trapped by the cell. Tapping on the cell generally dislodges any trapped bubbles. Bubbles left in the cell quickly resulted in a flow pattern, evidenced by visual inspection of the resulting deposit (Figure 3.5). The solutions were thoroughly degassed, using the blow-off of a high-pressure tank of liquid nitrogen, and were thus saturated with nitrogen.

In these studies, the flow rates were 55 mL/minute, and the pumps were run for 1.5 sec, resulting in about 1.4 mL of total solution pumped. Each element was deposited for 20 secs., quiescently.

In order to avoid problems with oxygen, the pump heads and the valve block were placed in a sealed Plexiglas box, and purged with the same nitrogen used to degas the solutions. All solutions were purged with nitrogen before and during deposition, and solution delivery tubes, leading from the solution reservoirs to the pumps, were encased in the Plexiglas box or double sheathed to prevent oxygen uptake. This outer sheath allowed the actual solution delivery tubes to be surrounded by a nitrogen "jacket" (Figure 3.1). The solution reservoirs were glass bottles, plumbed using PEEK and Teflon tubing. A separate peristaltic pump was used for each solution line, each one feeding into a common distribution valve and from there to the flow cell (Figure 3.4). The pumps (Cole Parmer) were run at 55 mL/min (30 RPM), and the distribution valve (NResearch) consisted of a Teflon block with four discreet solenoid controlled inlet lines and one outlet.

Figure 3.5. Bubble anomalies, or artifacts of bubbles that became trapped in the flow cell at some point during the EC-ALE process. Different magnifications are illustrated.



Solutions were prepared using reagent grade or better chemicals and deionized water from a Nanopure water (18 M Ω) filtration system. The filtration system was fed from the in-house deionized water system. Initially, there were some problems with the growth of bacteria in neutral solutions that were stored too long. Under the microscope, what looked like "spaghetti" was left on some deposits (Figure 3.6). A UV attachment for the Nanopure water system was subsequently installed, and, more importantly, timely preparation and usage of solutions was instituted, which eliminated the problems. All cadmium solutions consisted of 5.0 mM CdSO₄, pH 5.7, buffered with 50 mM acetate, and using 0.5 M Na₂SO₄ as a supporting electrolyte. Tellurium solutions were all 0.05 mM in TeO₂, and also used 0.5 M Na₂SO₄ as a supporting electrolyte. The Te buffers were variable; depending on which solution was used (either pH 10.2 or 2.0), being either 10 mM perchlorate or H₂SO₄. Various blank rinse solutions were also utilized, ranging from unbuffered 0.5 M Na₂SO₄ (pH ca. 6.0) to 0.5 M Na₂SO₄ buffered to have a pH analogous to its respective deposition solution.

The substrates used initially in these studies consisted of commercial Si(100) wafers, coated with 10 nm of Ti by thermal evaporation, followed by 200 nm of Au. The substrates were not annealed or heated prior to or during deposition. They appeared optically flat, mirror like, but actually consisted of ca. 40 nm Au "bumps", as observed with atomic force microscopy (AFM) (Digital Instruments Inc, Nanoscope III) (Figure 3.7a). These substrates were less than optimal, as the small atomic terraces that make up the Au "bumps", each a few Au atoms wide, make it difficult to form single crystalline deposits of any reasonable size. In order to improve substrate quality, microscope slides

Figure 3.6. A picture of a "spaghetti" anomaly as it is seen through an optical microscope at 125X. UV water sterilization and timely solution preparation solved this problem.


Figure 3.7: 3.7a is an AFM image of a commercial Au on Si substrate that is wholly unsuitable for EC-ALE due to the presence of 40 nm. bumps on the surface that preclude epitaxial deposition. 3.7b is an AFM image of an annealed, in-house produced Au on glass substrate. Note the different height ("z") scales in the images. The atomically flat planes seen in 3.7b are amenable to the EC-ALE modus.



were used, each having a 10 nm Ti cladding layer, followed by 400 nm of thermally evaporated Au. The Au was vapor deposited with the substrates hot, about 400 °C, and flame annealed before use. Figure 3.7b illustrates the improved quality of these substrates.

The ellipsometer was made by Sentech and used a HeNe laser at 632 nm. The angles of incidence and detection were adjustable, allowing measurement of sets of data at different angles and thus accurate determination of the thickness and/or optical constants. X-ray diffraction (XRD) was performed using a Scintag 2000 diffractometer equipped with a Cu source. A thin film attachment for the diffractometer allowed higher resolution on the detector. Standard spectra were obtained from the JPCDS database, using the Sun workstation to control the diffractometer. A Joel electron probe was used for electron probe microanalysis (EPMA). Optical microscopy was performed using a Jenavert metalographic microscope.

RESULTS AND DISCUSSION

THE CYCLE PROGRAM:

An EC-ALE cycle involves the sequential formation of atomic layers of each element by UPD. That an atomic layer of a less noble element can be reduced onto a more noble element at an underpotential is tractable. However, it should be thermodynamically impossible to underpotentially deposit a stable atomic layer of a more noble element on a less noble element. In the case of CdTe, Te (the more noble element) can be reductively deposited on Au at an underpotential from a pH 2 $HTeO_2^+$ solution at 0.1 V (Figure 3.8b). The solution can then be exchanged for a CdSO₄ solution, and Cd

Figure 3.8. Cyclic voltammograms of basic Te (3.8a), acidic Te (3.8b) and Cd (3.8c) are shown. A UPD of Te layer deposited from the acidic solution (3.8b) is not stable if at potentials required to deposit UPD Cd (3.8c)



(Figure 3.8c, the less noble element) can be underpotentially deposited on the Te atomic layer at -0.7 V (Figure 3.8c). The potential must be then shifted back to 0.1 V to reductively deposit an atomic layer of Te on the Cd, but at 0.1V the previously deposited Cd is no longer stable and oxidatively strips from the surface.

In early studies [4,39-42], this problem was circumvented by using the following equilibrium (Figure 3.8, a and c):

$$HTe^{-} \ll Te_{(UPD)} + 2e^{-} + H^{+}$$
 {1},

which is described here as oxidative Te UPD. One problem with using eq. {1} is that the E° for Te/HTe⁻ reduction is about -1.14 V vs. SHE, so that aqueous solutions of HTe⁻ are not stable. However, the equilibrium between Te and HTe⁻ was still used (without solutions of HTe⁻) by first depositing Te_{UPD}, along with a small amount of bulk Te, from a stable HTeO₂⁺ solution. The deposition was carried out at an overpotential where Cd on the surface was stable:

$$2HTeO_2^+ + 6H^+ + 8e^- = = Te_{(UPD)} + Te_{(Bulk)} + 4H_2O$$
{2}.

The HTeO_2^+ solution was then exchanged for a blank electrolyte solution, and a potential sufficiently negative to reduce $\text{Te}_{(\text{Bulk})}$, but not to reduce $\text{Te}_{(\text{UPD})}$ off of the surface, was applied

$$Te_{(UPD)} + Te_{(Bulk)} + H^+ + 2e^- ==> Te_{(UPD)} + HTe^-$$
 {3}

Figure 3.9. Shown is one of the many possible operational models for the EC-ALE formation of CdTe. This cycle deposits an atomic monolayer of Te oxidatively, so a stripping step to remove bulk Te is required.



leaving $Te_{(UPD)}$ on the Cd covered electrode. This program is diagramed in (Figure 3.9). Te is deposited at -0.7 V, followed by solution exchange for a blank, and the potential is shifted to -1.1 V to reduce bulk Te. Good quality deposits were obtained using this program, but as mentioned in the introduction, the growth rate was only 0.4 ML/cycle, as opposed to the anticipated 1.0 ML/cycle [39, 40]. The deposits were stoichiometric (EPMA). The low coverages may have resulted from loss of potential control with each rinse, a shortcoming in the H-cell design.

In addition to the deposits being thinner than expected using the program in (Figure 3.9) and the H-cell (Figure 3.3), when that program was combined with a thin layer flow cell (Figure 3.4), clusters of crystallites (rocks) of 30-50 µm size (Figure 3.10) were observed after 200 cycles of deposition. The rocks were few and randomly distributed across the deposit. From EPMA they appeared to be predominately Te, while the flat surrounding areas were stoichiometric CdTe. The rocks grew only at certain sites on the substrate. As Te deposition was a two-step process (Figure 3.9), the rocks may have resulted from problems with either step. The rocks could result either from excess Te deposition at these sites during the Te deposition step, or from the incomplete reductive removal of bulk Te during the stripping step.

A number of different cycle steps (Figure 3.9) were adjusted to determine if the rocks could be avoided using the old cycle. For instance, if the rocks were the result of incomplete dissolution of the bulk Te, longer stripping steps, more reductive potentials, and/or increased rinsing should limit their growth. The rocks remained, however, with little change in appearance, while the CdTe deposits as a whole were thinner. It is

Figure 3.10. Clusters of crystallites (rocks) of 30-50 μm size .



/_{ca. 50 μm}

probable that the rocks were formed on defects in the Au films, which were the commercial Au on Ti coated Si(100) substrates. AFM images in (Figure 3.7) show the of the Au on Si(100) (Figure 3.7a) as well as a Au film formed on glass that was annealed in an H_2 flame (Figure 3.7b).

A new cycle was subsequently developed for the flow cell (Figure 3.4), with emphasis on simplifying the process as much as possible (Figure 3.11). In its most abbreviated form, only two solutions and one potential were used. Atomic layers of both reactants were reductively deposited directly from their precursor solutions at -0.7 V. No bulk reductive stripping step was included.

Figure 3.8b shows typical voltammetry for a Au electrode in a pH 2.0 solution of $HTeO_2^+$. There are three reductive voltammetric features, the first peak at +0.4V for Te UPD results in the formation of about 1/3 ML (one ML being defined as one adsorbate atom for each Au surface atom) [46-52]. The next reduction feature, a shoulder at +0.10V, also appears surface limited, resulting in a total coverage of 4/9 ML. The third reduction feature, at -0.30V, is the onset of bulk Te deposition.

The formal potential for $HTeO_2^+/Te$ appears to be about 0.5V, suggesting that the surface limited peaks (Figure 3.8b) occur at overpotentials, and that the deposition process is kinetically slow, especially considering the scan rate was only 5 mV/sec. Studies by this group indicate that the kinetics for Te deposition are slowed even more as solutions are made more basic. This is evidenced by a significant increase in the peak splitting of deposition and stripping features (Figure 3.8a) for the electrode in a pH 10.2 solution of $HTeO_3^-$, as compared to the pH 2 solution. Similar surface limited features are evident prior to bulk deposition in the pH 10.2 solution, corresponding to a total

Figure 3.11. Shown is one of the many possible operational models for the EC-ALE formation of CdTe. This truncated cycle deposits an atomic monolayer of Te reductively, and deposits both Te and Cd at -0.70V. No rinse is included between species.



coverage of about 0.43 ML. The fact that bulk Te deposition does not occur until –0.70 V in the pH 10.2 solution suggests that surface limited atomic layers of Te might be formed at potentials in the range of –0.6 to -0.7 V, the same potential range used for Cd UPD from a pH 5.7 solution (Figure 8c). These results prompted the new cycle where both elements were reductively deposited (Figure 3.11).

As noted above, the simplest new cycle involved reductive deposition of both elements (Figure 3.11) at a constant potential, using only two solutions (no rinse), and no stripping step. Without rinsing, however, some codeposition is inevitable, as both element precursors will be present in the cell simultaneously as the solutions are exchanged. To minimize codeposition, the systems were allowed to go open circuit during solution exchange, and potentials were only applied when the pure solutions were in the cell. Possible problems with the open circuit condition have been discussed. Good deposits were formed in this manner, however. Some Cd(OH)₂ was formed in the cell during rinsing, appearing as a white, flocculent, precipitate on the down stream side of the cell. Obviously, this was the result of mixing the pH 10.2 HTeO₃⁻ solution with the pH 5.7 CdSO₄ solution.

To avoid problems with codeposition, to maintain potential control throughout the cycle, and to avoid $Cd(OH)_2$ precipitation, the cycle was modified by addition of a single rinse. In the old cycle programs [39-41], two rinse solutions were used: one for each reactant solution. Each blank included everything the reactant solution contained except the reactant. In the present modification, a single, common, unbuffered blank solution was used between each Cd or Te containing solution. The absence of buffers in the rinse allowed the buffers in the reactant solutions to control the pH, while the rinse simply

flushed out the previous aliquot of deposition solution. Thus potential control could be maintained throughout the cycle, and the Cd(OH)₂ formation was avoided. Foresti et al. matched the pHs of both reactant solutions and the blank in their studies of CdS formation using EC-ALE. Basic solutions of sulfide ions where alternated with basic solutions of cadmium ions. To keep the Cd^{2+} from precipitating as $Cd(OH)_2$ at such high pH values, pyrophosphate was used to complex the ion [53]. Te was deposited at -0.70V, while Cd was deposited at -0.60V, and no bulk Te stripping step for bulk Te was used (Figure 3.12) in this single rinse solution cycle. EPMA indicated that these deposits were stoichiometric, and the deposition rate was 1ML per cycle. However, the clusters of crystallites (rocks) of 30-50 µm size (Figure 3.10) persisted. Figure 3.13 is a graph of the coverage as a function of the number of cycles. The linear behavior expected for a surface limited deposition process is observed. The slope of the graph is 1.03ML/cycle, or 37.6 nm/cycle, very close to the 1 ML/cycle, or 37.4 nm, expected. The thickness measurements in (Figure 3.13) were made using ellipsometry, based on the optical constants for CdTe. Deposits in this series exhibited the literature bandgap for CdTe. Figure 3.14 is a plot of IR absorption data from a 200 cycle CdTe deposit. The data was obtained using the uncoated Au substrate as a background. The source was incident at the Brewster angle for CdTe to minimize dispersion (Figure 3.15). The band gap was then determined by plotting $(\alpha h v)^2$ vs. the energy in eV (Figure 3.14). Extrapolation of the linear portion suggests a band gap of 1.55 eV, in excellent agreement with literature values of 1.58 eV. At that point, the group switched from using commercial Au on Si substrates (Figure 3.7a) to using in-house produced Au on glass substrates

Figure 3.12. Shown is one of the many possible operational models for the EC-ALE formation of CdTe. This cycle deposits an atomic monolayer of Te reductively, deposits Te and Cd at different potentials, and uses a single rinse solution between species.



Figure 3.13. A plot of CdTe EC-ALE deposit thickness versus the number of cycles deposited.



Figure 3.14. Extrapolation of a plot of IR absorption data yields the bandgap for EC-ALE CdTe. The experimental value of 1.55 ev is in excellent agreement with the literature bandgap of 1.58 ev.



Figure 3.15. Illustration of the method used to determine the bandgaps of EC-ALE deposits. The response of the Au substrate is subtracted from the film measurement. The incident IR energy is scanned at the Brewster angle until transmittance is seen. At energies below the bandgap, all incident energy will be absorbed.



(Figure 3.7b), allowing a plot of the thicknesses and stoichiometries for a series of 200 cycle deposits to be obtained (Figure 3.16). The Cd deposition potential was held at -0.7V while the Te potential was shifted from -0.8 V to 0.1 V. Deposits formed at potentials above -0.1 V looked like the pristine substrate, with no significant deposit detected visually or by ellipsometry. As the potential was shifted negatively to -0.1 V, there was an abrupt increase in coverage, up to 57 nm. A 200-cycle deposit should be 74.8 nm thick, assuming one monolayer of CdTe (grown with a (111) orientation) [40,41] is produced each cycle. Thus the deposit formed at -0.1 V corresponds to 0.76 ML/cycle, and displayed a silvery blue color. As the potential was shifted more negative, the coverage increased gradually until a 78 nm thick deposit (1.04 ML/cycle) resulted. This deposit was formed with Te deposited at -0.5 V and displayed a gold color, similar to the color of the substrate. Deposits of similar thicknesses and color were formed using potentials as low as -0.7 V, but at -0.8 V, the deposits became much thicker and rougher. Through the optical microscope, the Au on glass substrates appeared optically flat, with few features evident, even at 1000X magnification. Good deposits, in the plateau region of (Figure 3.16), showed similar morphologies. However, for the deposits formed at -0.8V and more negative, "sand" was observed by optical microscopy (Figure 3.17). That is, the deposit was reminiscent of a "sandy beach". The initially flat homogeneous substrates now evidenced a multicolored speckled surface when viewed at 1000X. Experience has shown that when the conditions are pushed to the point where more than an atomic layer is deposited in a cycle step, 3-D growth is initiated, and 200 cycle deposits generally look sandy (Figure 3.17).

Figure 3.16. A plot of deposit thickness versus the Te deposition potential used in the EC-ALE cycle is shown. Stoichiometric data is also displayed. The wide plateau of 0.6V, where changing conditions had minimal effect on the deposit, is indicative of a surface limited process such as UPD. The Cd deposition potential was held constant at – 0.60v in this study.



Figure 3.17. A nice EC-ALE CdTe deposit is seen in 3.17a, while a "sandy" deposit is seen in 3.17b. Both images are photographs taken through an optical microscope at 1000X.







b

Ellipsometry on roughened surfaces is difficult, given that the measurements are based on the assumption of a flat surface [54]. Subsequently, an accurate deposit thickness cannot be obtained on deposits formed at potentials of -0.8 V or lower, given the roughness. The probable reason for the roughening at -0.8 V is evident from (Figure 3.8a), as bulk Te deposition begins at potentials below -0.7 V. For potentials less than - 0.7 V, more than a monolayer of Te is deposited each cycle, effectively inducing more than a monolayer of Cd to deposit in each cycle. Similarly, depositing Te under mass transfer limited conditions, as opposed to surface limited conditions, results in some 3-D growth and sand. This is inevitable, as the precepts of ALE no longer apply to the deposition process.

The rocks, or clusters of Te crystallites (Figure 3.10), were not seen in deposits formed with a Te deposition potential in the plateau region when using the new substrates. It appears that the rocks may have resulted from defects in the Au layers on the Ti coated Si(100) substrates. Possibly Te deposition was accelerated at these points, and some electrical characteristic of the defect prevented the subsequent dissolution of the excess Te. Overall, the Au on glass substrates were much smoother (Figure 3.7b), exhibiting atomically flat planes as large as several hundred nm. Best of all, they did not produce the Te crystallites (rocks).

For deposition potentials of 0.0 V and positive, essentially no deposition was observed. As indicated in (Figure 3.8a), no deposits would be expected until potentials of -0.3 V or lower are reached, since the first Te UPD peak does not occur until -0.25 V. Despite this fact, (Figure 3.16) clearly shows that deposits were formed when -0.1 V was employed as the Te deposition potential. Figure 3.16 is not necessarily an accurate

representation of the conditions for Te deposition during ALE, as it depicts Te deposition on Au, not Te deposition on Cd. The occurrence of Te deposition at such a high potential may be the result of faster kinetics on the Cd surface. Increased stability on the Cd surface may also be a contributing factor. Evidently, the Cd atomic layers deposited at – 0.7V do not strip at –0.1V while the Te is being deposited. This alludes to a greatly increased stability of the Cd on Te, as compared to Te on Au. Previous studies showed that Cd begins to strip from CdTe single crystals at potentials near –0.1V in mild acid [56], consistent with the results shown in (Figure 3.16). The most notable feature of (Figure 3.16) is the nearly constant coverage, despite the fact that the potential for Te deposition is shifted by 0.6 V. This result clearly suggests that the deposition is surface limited, obviously not controlled either by electrode potential or by mass transfer to the electrode surface.

Figure 3.18 shows a similar experimental series in which the Te deposition potential was held constant at –0.650V, while the Cd deposition potential was varied as indicated. Electron probe microanalysis of the deposits showed them to be essentially stoichiometric except at potentials below –0.7V (Figure 3.16). There is a short plateau region, between –0.45 and –0.7V, where the coverages are nearly 1 ML/cycle, but show some increase with decreasing Cd potential. Below –0.7V the coverage increases rapidly as bulk Cd begins to form. Essentially, 3D growth takes over and the deposits become sandy. Above –0.45V, the coverage drops radically, while the stoichiometry remains close to one, but slightly rich in Te. Overall, the deposits appear significantly more

Figure 3.18. A plot of deposit thickness versus the Cd deposition potential used in the EC-ALE cycle is shown. Stoichiometric data is also displayed. The plateau of 0.1V, where changing conditions had minimal effect on the deposit, is indicative of a surface limited process such as UPD. The Te deposition potential was held constant at -0.650v in this study.



CdTe Deposit Thickness and Stoichiometry (Ratio Cd / Te) vs. Cd Deposition Potential

sensitive to the potential used for Cd deposition than to those chosen for Te deposition. From the standpoints of stoichiometry and coverage per cycle, the best deposits appear to be where the Cd was deposited at -0.6V. These are the same conditions used to form (Figure 3.16).

Visual inspection of the deposits that were used to construct (Figures 3.16 and 3.18) indicated a lack of deposit homogeneity. That is, good quality deposits would often only cover part of the substrate, while some areas appeared to have no deposit, while still other areas appeared black. The black areas were sandy, suggesting too much deposition. The most pernicious problem was lack of deposition near the cell ingress (entrance). Overall, this inhomogeneity seemed to be an artifact of fluid flow patterns. The geometry of the early generation flow cells, such as those used to collect (Figures 3.16 and 3.19), dictated a 90° turn of the solution at the cell ingress. This likely resulted in significant turbulence near the entrance, which could well explain the fallow ingress.

These results have been difficult to explain, but appear to be related to two issues. Primarily, if too much Te is deposited, the deposit appears to become pacified. That is, no further deposit can form if several ML of bulk Te are initially deposited. The second issue is that, as noted above, Te deposition is quite irreversible. The peaks in (Figure 8a) appear to be UPD, but they actually occur at over potentials. The process only appears surface limited due to the slow deposition kinetics. Some bulk Te is deposited as the first atomic layers form. Given homogeneous conditions in the cell and the application of correct potentials, atomic layers of Te can be reproducibly deposited by reductive deposition. Conversely, if flow through the cell was not homogeneous and laminar, areas of varied turbulence could be more or less amenable to increased deposition and overgrowth. This may explain the lack of deposit at the cell entrance. Extra Te deposition in those areas very early in the experiment could, in effect, cause localized pacification of the substrate, precluding any further deposition in these electrically "dead" areas.

Frequently, the deposit looked fine a few mm downstream of the ingress, as laminar flow was established in the cell by that point. To help test this turbulence hypothesis, the first third of a substrate was coated with a thin layer of resist (finger nail polish) to prevent deposition near the entrance. The resulting deposit began cleanly where the resistive coating terminated, suggesting that laminar flow was indeed established while the solution flowed over the resist coated part of the substrate. This is why good quality deposits have been formed downstream. In recent flow cells (Figure 3.4) the 90° turn has been limited to only ca.30°, hastening the establishment of laminar flow in the solution run.

The variation within the cell further suggests a flow dependence that should not be present with a truly surface limited process. This again suggests the error of thinking that Te deposition from the basic solution (Figure 3.8a) is a thermodynamically surface limited process. Evidently, undeposited areas of the substrate were the result of excessive Te deposition and pacification very early in the cycle. This is likely an artifact of localized turbulence variations at the cell inlet, as these convection vagaries could make Te overgrowth more facile. Sandy areas, however, were the result of too much Te being deposited within each cycle; not enough to form a passivating Te layer, but enough for the growth of a Te rich film which appeared sandy and exhibited 3-D growth. It is interesting to note that the same loss of deposit at the cell entrance was not observed for deposits of CdSe, even under very analogous conditions [56], or for a number of other compounds formed using the same EC-ALE hardware. Te appears to be somewhat of an enigma. No doubt its vagaries are the result of both its significant irreversibility and its predilection for forming passive films. Studies of ZnTe growth using EC-ALE are beginning, and should help in understanding this issue.

As an attempt to correct problems with inhomogeneity and 3-D growth in the deposits, resulting from problems with excess Te deposition, the cycle was modified to include the Te bulk-stripping step (Figure 3.19). In addition, two pH matched blanks were used, one equivalent to the Te solution and one equivalent to the Cd solution. This cycle involves initial reductive deposition of a Te layer at -0.70V, followed by a stripping step at -1.0V in the Te blank solution. This cycle is very similar to that used previously with the H-cell geometry (Figure 3) [40,41]. Deposits formed with this program exhibited significantly improved homogeneity. That is, the deposit covered the whole substrate, with essentially no evidence of flow patterns. Figure 3.20 is an X-ray diffraction pattern for a 200-cycle deposit using the program in (Figure 3.19). Peaks for Au are well defined, while peaks at ca. 24, 39 and 44 degrees for zinc blende CdTe are also evident. The (111) reflection is most prominent, indicating some preferential growth, according to the JCPDS database. The pattern is very similar to that obtained previously for CdTe films grown with the old cycle (Figure 3.9) and H-cell [40]. EPMA results for these deposits were as expected, indicating the formation of stoichiometric CdTe.
Figure 3.19. This example, the longest of the EC-ALE cycles, produces the best deposits. It requires not only a step for stripping away excess Te, but also needs two blanks, each having its pH matched to its respective deposition solution.



Figure 3.20. Glancing angle X-ray diffraction for EC-ALE CdTe is shown. Peaks for Au are well defined. Peaks at ca. 24, 39 and 44 degrees for zinc blende CdTe are also evident. The (111) reflection is most prominent, indicating some preferential growth.



One of the issues becoming apparent in the formation of compounds using EC-ALE is that the potentials determined by analyzing voltammograms, such as those shown in (Figure 3.8,a-c), are not necessarily the final word in experimental conditions. These simplified conditions certainly do not depict the optimum parameters for every cycle in the experiment. Generally, if potentials for the deposition of atomic layers on Au are used from the beginning, the initial deposition is excessive, but then the deposition currents and the amounts of deposited material quickly decrease. Ultimately, no observable deposit results (Figure 3.21). Therefore, in the deposits described above, more negative potentials were generally used. The drawback has been that during the first few cycles, before steady state conditions take over, more than a monolayer was deposited each cycle (Figure 3.21). As more than a monolayer is deposited for each of the first few cycles, some 3D growth is expected. Thus the quality of the deposits must be at least partially limited by the morphology resulting from these initial cycles. On the other hand, if potentials that will produce a monolayer, as determined by coulometry in the flow cell, are used from the beginning, the initial layers are close to one monolayer, but the deposition again quickly drops away to nothing (Figure 3.22)

A solution being practiced with the deposition of most compounds by EC-ALE with this group is to change the potentials from cycle to cycle, usually over the first 30 cycles. After about 30 cycles, the potentials have reached steady state, and no further changes are necessary, regardless of how thick you intend to grow the electrodeposit. In this way, the desirable deposition of single atomic layers of the constituents each cycle is more tractable. The procedure is to use a hypothesis (an educated guess) regarding the potential changes that will be needed, and good programs can frequently be produced in Figure 3.21. If deposition potentials indicated by cyclic voltammograms of Cd or Te on Au are used from the start of the EC-ALE cycle, excessive overgrowth occurs at first, but then the deposition quickly decays to a negligible amount.



Figure 3.22. If deposition potentials indicated by coulometry in the flow cell are used from the start of the EC-ALE cycle the first layers come close to one monolayer, but then the deposition quickly decays to a negligible amount.



this way after a few iterations. Ideally, the resulting currents could be used in a feedback loop to allow such determinations and adjustments to be executed in real time, on the fly, so to speak. This has, however, proven to be difficult. The main issues are that some

oxygen is generally present, even given the extensive purging that is being used, and hydrogen evolution can occur at these potentials. In addition, frequently the charges do not completely make sense. That is, if you put down a ML of Cd, and then a ML of Te, you would expect that the charge for the Te would be twice that for formation of the ML of Cd. This is the result of Cd²⁺ reduction being a two-electron process, while HTeO₂⁺ reduction requires four-electrons. Experience, however, has shown that these charges are seldom what would be expected from this simple model. It appears that in some cases, extra Cd is deposited, as the Cd charge is greater than that for Te. However, the deposit does not turn out to be Cd rich, as this would suggest. Instead, these deposits are stoichiometric CdTe. This suggests that the excess Cd may be oxidized concurrently with the reduction of some Te, producing the correct end result of stoichiometric deposits. Careful studies of these reactions are underway using EQCM.

CONCLUSIONS

This article describes the formation of CdTe deposits by electrochemical ALE (EC-ALE) using a new cycle program and a new flow cell. The new cell uses a silicone gasket and produces a $1X3 \text{ cm}^2$ CdTe deposit with a minimum of solution. In addition, potential control is maintained during the entire deposition cycle. The new cycle is the result of the realization that by using basic tellurite solutions, an atomic layer of Te can be formed either oxidatively or reductively, depending on the program variation chosen.

Either approach can produce CdTe having the correct stoichiometry and bandgap. While the use of reductive UPD eliminates the step of stripping excess Te, greatly simplifying the cycle, the best deposits were generally formed employing the more complex cycle and oxidative Te UPD formation. This more complicated program also eliminates many of the unknowns in the process, facilitating a more accurate characterization of the first few layers of deposition, leading to better understanding and to the implementation of more stringent control over this keystone element of the process.

The resulting deposits are formed at a rate of 1 ML/cycle, as opposed to previous studies where only 0.4 ML/cycle was obtained. Good quality deposits were maintained at growth rates up to 1 ML/cycle, while growth rates in excess of 1 ML/cycle resulted in 3-D growth and roughening as evidenced by optical microscopy. The reasons for the improved coverage/cycle are probably related to the rinsing procedures. The amount of rinsing used in previous work [40] was excessive, possibly leading to some loss of Cd while solutions were exchanged, a problem that could only be exacerbated by the loss of potential control during the rinse.

In studies of the dependence of deposit thickness on the potential used to form Te atomic layers, a 0.6 V wide plateau was observed. This is to be compared with the 0.1 V plateau observed using the previous cycle and deposition cell [40]. This is very encouraging, as it suggest flexibility in the conditions chosen to achieve layer-by-layer growth.

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CHAPTER 4

CONCLUSIONS AND FUTURE STUDIES

I believe future studies with EC-ALE should meld with ongoing work, while at the same time be directed towards scale up of the modus. EC-ALE can supplant the conventional semiconductor fabrications methods. But absolute proof of concept, that is constructing a simple device having significant energy conversion efficiency, is a must. To meet this goal, more must be learned about the finer points of electrochemical atomic layer epitaxy, many of which I will discuss below. Also, experiments to validate the prospect of scaling up the methodology are definitely in order. I feel that work in both these areas could proceed concomitantly.

The state of research calls for a collaboration at this time. The input of a researcher that is part engineer, part chemist, and part physicists is the order of the day. Much effort has been expended in developing and testing new EC-ALE hardware, and that trend will not cease. However I do feel the equipment development has peaked, that is, we are very close to the point of diminishing returns in that area. The tack to pursue now is fine-tuning the apparatus even more. This is where we need the flow "expert" to modify and or optimize the flow cell. In simplest terms, I would like the flow cell to satisfy two requirements. First, we need a design in which the flow is as laminar as possible. Second, that design needs to be readily enlarged (or miniaturized, possibly) without experiencing reduced efficacies. The idea is that the size can change so long as the various aspect ratios of the design do not. EC-ALE has proven its ability to go where other electrodeposition methods cannot, as in depositing InAs on the inside of a copper tube. Now let's further demonstrate the versatility of EC-ALE by proving a scaling ability.

I would like to attach this "perfect" cell to a new deposition system. The basic equipment would be no different from that in place now, but a few modifications would be in order. I would essentially like to build a "test bed", a system with the adaptability necessary to investigate many of the variables of the EC-ALE process. Many of these questions have been discussed at length in the group; and rudimentary experimental steps have already ensued to answer some of them.

Aside from the attributes mentioned above that make my consummate flow cell a reality, the cell needs a couple of more tricks in its repertoire. For starters, the ability to make multiple working electrode connections is a must. I think that we could now produce substrates having at least four electrically isolated areas, essentially forming four separate working electrodes. Much experience has been gained with the lab's vapor depositor, and a single experiment in which a bifurcated electrode was both produced and employed as an EC-ALE substrate has been completed by Travis Wade (Figure 5.1). Couple this idea with four separate potentiostats, interface the system so that each potentiostat, and thus each separate electrode, has independent control and electronic data collection. This system presents a myriad of possibilities to ferret out the unknowns of deposition in the flow cell. So much of my work has been tainted by the presence of flow patterns and the lack of homogeneity in deposits, and this could address many of those issues. This also takes the first steps at bringing an item of many group discussions to fruition, that of producing an "array" of semiconducting structures on a single substrate. This cell would also need to accept at least one more addition to the flow channel, a pH electrode. So many questions about the need for pH matched solutions and how the pH actually changes in the cell under experimental conditions have pervaded my efforts.

Figure 5.1. Proof of concept for producing sectioned electrodes is shown. An in-house produced substrate having one annealed side and one unannealed side was employed as an EC-ALE substrate. Absorbance data clearly indicates a difference in the quality of the two substrate sections.



Experience only provides me with a first approximation in reference to this; that widely varying pHs are trouble. At the same time, I know that such conditions can work. Not knowing the specifics of this conundrum is the impetus for the pH studies. Also, a dissolved oxygen sensor in the flow channel would be useful. The need to know just exactly how low the oxygen content of solution must be before EC-ALE can succeed, a solution that is actually in the cell and exposed to EC-ALE, is imperative to any scale up considerations. This route is being undertaken even now in the lab. A suitable pH electrode has been purchased, and basic drawings of a cell design that would accept the addition have been produced. This design could also accept a dissolved oxygen sensor.

Expounding on the idea of a "test bed" system, variable speed pumps are needed. We could use the same genre of pumps that are mounted now, with variable speed controllers. I undertook some cursory steps in this direction by investigating different flow rates by changing tubing sizes at the pump heads (Figures 5.2 and 5.3). But the range of accessible flow rates is limited by this approach, and more finite control of pump RPMs is required for the collection of any meaningful data and reproducibility. Again, many questions about flow rates persist in the EC-ALE technique. How do changes affect the physics of laminar flow? How do changes in these parameters affect the electrodeposition process? What about the question of which is better, laminar flow or turbulent flow? Laminar flow allows us to sweep the cell clear of one reactant before introducing another more readily, thus avoiding codeposition, but turbulent flow surely enhances convection in the cell, thus impacting exchange current and EC-ALE's way of getting ad atoms to optimal sites in lieu of the classic, heat spurred surface diffusion. Its likely that some compromise of these two

Figure 5.2. Preliminary rinsing studies of the EC-ALE hardware plotting monolayers of Te stripped versus the number of cell volumes exchanged.



Figure 5.3. Preliminary rinsing studies of the EC-ALE hardware plotting monolayers of Cd stripped versus the number of cell volumes exchanged.



views is the ultimate answer. Can we find that "sweet spot"? Only extensive work, with a highly adaptable system, can extricate these answers.

I would like to say a few words about substrates. In terms of demonstrating the versatility of the technique, any study that forms EC-ALE deposits on different substrates would be desirable. Ultimately, I would hope that new insights into optimization, possibly gained through some of the experiments I have suggested, would allow a return to silicon wafers as substrates. This would go a long way in making EC-ALE more attractive to industry. The use of any substrate that would be lattice matched to the growing compound would be a definite advantage, but I think that ultimately the technique must find ways to circumvent this specter. To have more universal appeal, EC-ALE must be able to adapt, improvise and overcome the lattice matching issue. This can be accomplished by modifying substrates, possibly by electrodepositing a thin cladding layer of one compound that is more amenable to accepting the major compound that is to be electrodeposited, thus mediating the difference in lattice parameters.. An alternate route that I have often considered is a hybrid method. The lattice matching issue boils down to getting the first few ad layers correct. The closer to perfect the initial layers are, the fewer defect-inducing strain relief mechanisms will be necessary to maintain structural integrity in the film. My experience tells me that few issues on the edge of the envelope are cut and dried. The real answer is often found somewhere between the extremes. This thinking forces me to be optimistic about the prospects of hybridizing EC-ALE with a more conventional technique. If MBE or VPE or codeposition or whatever could be employed to deposit the "best possible" structure for the first 15-20 monolayers, what could EC-ALE do as far as completing the deposit up to any desired

thickness? Would the use of additives, such as those employed in the dual damascene technique, be tractable? I believe that EC-ALE could really shine in this endeavor, perhaps beating the odds and surpassing any single method deposition technique out there.

Perhaps the most insipient of all future studies is that of investigating the latent intricacies of EC-ALE with electrical quartz crystal microbalance (EQCM) studies. My nemesis has been the inability to reconcile disparities in coulometry data. Data collected under UHV conditions is marginally dissimilar to that seen in the flow cell. Analogously, data collected with a TLE also diverges slightly from both UHV data and flow cell data. The one tool that can assimilate this data is the EQCM. These studies are now underway in the lab.

Finally, the general trend of expanding the range of compounds that can be formed by EC-ALE must continue. The past few years has seen work in the lab divagate from the exclusive investigation of II-VI compounds to include III-V compounds as well. In this same vein, work to produce superlattices should also proceed. Figure 5.4 shows my cursory attempts a producing a CdTe/ CdSe Superlattice. This first attempt in the Stickney lab in this direction shows much promise. The possibilities here are virtually unlimited. New opportunities in this direction present themselves almost daily as researchers learn more about bandgap engineering. I believe this growing body of knowledge will always harbor a niche that only EC-ALE can occupy.

Figure 5.4. The first attempt at producing a superlattice with EC-ALE is shown at 1000X as viewed through an optical microscope.. This superlattice is a total of 1044 layers thick, having a repeat unit of 2 layers of CdTe and 10 layers of CdSe.

