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Electrochemical Atomic Layer Deposition (EC-ALD) Low Cost Synthesis of Engineered Materials a Short Review

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Abstract

Having mastered the technology of epitaxial deposition of crystalline thin films (i.e. homo and heteroepitaxy) on crystalline substrates has already been found providing better device designs with numerous advantages in the development of microelectronics devices and circuits. Consequently, mass-scale production of epitaxial thin films could successfully be developed and used in fabricating discrete devices and integrated circuits (ICs) using silicon/compound semiconductors commercially. Especially, realizing the hetero-epitaxial interfaces possessing two-dimensional electron/hole gas (2DEG/2DHG) sheets could offer very-high electron/hole mobilities for producing high-electron-mobility transistors (HEMTs) and amplifiers for microwave/millimeter-wave communication systems. However, the major limitation of this technology was its requirement of extremely high cost infrastructures. Subsequently, the rising demands of the technologies to produce large-size displays/electronics systems, and large-numbers of sensors/actuators in Internet of Thing (IoT) made it imminent for the researchers to explore replacing the existing cost intensive technologies by more affordable ones. In such an endeavor, developing a simpler and alternate epitaxial technology became imminent to look for. Incidentally, electrodeposition based epitaxy attracted the attention of the researchers by employing potentiostatic set-up for understanding the growth kinetics of the ionic species involved. While going through these studies, starting with the deposition of metallic/semiconducting thin films, atomic-layer epitaxial depositions could be successfully made and named as electrochemical atomic layer deposition (EC-ALD). Despite numerous attempts made for almost two decades in this fascinating field the related technology is not yet ready for its commercial exploitations. Some of the salient features of this process (i.e. commonly known as EC-ALD or EC-ALE) are examined here with recent results along with future prospects.

Indexing Terms: *Vapor Phase Epitaxy (VPE), Liquid Phase Epitaxy (LPE), Atomic Layer Deposition, Atomic Layer Epitaxy (ALE), and Molecular Beam Epitaxy (MBE); Electrochemical Atomic Layer Deposition (EC-ALD)*

Introduction

A variety of thin over-layers have been produced commercially using chemical vapor depositions (CVDs) in the later half of the 20th Century for their extensive applications in microelectronics devices and integrated circuits of different complexities [1]. Out of numerous types of such thin films, those of monocrystalline semiconducting ones deposited after extensive refinement of the general CVD-processes were noted to play a significant role in extending the utility of crystalline substrates in realizing optimal functionalities from the fabricated devices and circuits [2]. Epitaxial growth in combination with oxide masking and diffusion has given the device designer extremely flexible tools for making an almost unlimited structural options. After 1964 epitaxial growth remained an important technique in semiconductor device fabrication and the demand for improved device yield per wafer, still higher device operating frequencies, and more sophisticated device structures did need continuing innovation and development [3-5].

While exploring better CVD processes, yet another improved version of atomic-layer deposition (ALD) was discovered to produce atomically thin layers that were put to use in producing discrete devices, integrated circuits (ICs), and photovoltaic solar cells with improved performances [6]. Further, the applications of various kinds of CVD thin films included many other forms of polycrystalline Si in photovoltaic devices, wear-resistant coatings of carbides/nitrides, in addition to incorporating hydrophobic, and weather-resistant features. Recently developed crystalline nanoporous materials using metal-organic frameworks (MOF) are expected to produce good gas sensors, and low-k dielectrics [7].

CVD-over-layers of monocrystalline semiconductors are deposited on to a substrate of the same or the other materials with almost matching lattice constant within few-percent come under the category of homo or hetero epitaxial thin films. Such semiconducting thin films in combination with those of the dielectric and metal thin films have been put to maximum use in realizing the required

doping profiles of a multi-layered device structures to sustain the corresponding electric field profile capable of offering the desired charge carrier transport across such structures [8].

In a typical thin film CVD, one or more gaseous precursors are mixed with a nonreactive carrier gas. Such compositions are allowed to pass over a heated substrate placed appropriately inside a reactor. These precursors react and/or decompose on the substrate surface resulting in deposition of the corresponding thin films. Volatile reaction by-products are subsequently removed from the reactor with the help of carrier gas used. The CVD over-layers so deposited included monocrystalline, polycrystalline, amorphous, as well as epitaxial thin films. These also included a big list of materials like various combinations of silicon (e.g. oxide, carbide, nitride/oxynitride), germanium, carbon as single/multi-walled nanotubes, graphene, and diamond; fluorocarbons; W, Ti, TiN, and various high-k dielectric materials, and many more [2,8].

In order to meet the structural specifications for producing the active device interfaces having targeted I-V characteristics, Si CVD was refined to the extent of depositing monocrystalline thin films in commercial high throughput reactors by taking right combinations of temperature, pressure, and appropriate silicon bearing precursors. This kind of vapor phase epitaxy (VPE) could be used in realizing specific combinations of the substrate along with a combination of over-layers using special deposition conditions including a typical design of reaction chamber, substrate holder, and the gas manifold to introduce different precursor species in gas phase. These reactant precursors diffuse from the flowing carrier gas stream and reach the heated substrate. Subsequently, they participate in chemical reactions producing atomic and molecular species that help in growing 2-D epitaxial thin film on the entire surface. A number of Si bearing chemical precursors that are often used in silicon epitaxy includes silicon tetrachloride ($SiCl_4$), di-chlorosilane (SiH_2Cl_2), tri-chlorosilane ($SiHCl_3$) and silane (SiH_4) [2,8].

Another variant of CVD epitaxy called molecular beam epitaxy (MBE) was subsequently added to the existing list of thin film depositions by considerably modifying the surface reaction conditions. For instance, thermal evaporations of the precursors were used to grow epitaxial layers instead of deposition through dissociation and chemical reactions employed in the conventional CVD process. Although, the method has been known since the early 1960s, it has only recently been possible to develop the production worthy processes meeting the requirements of silicon device fabrications in the manufacturing environment. In MBE process, the Si along with dopants are thermally evaporated from effusion cells before transporting them at a relatively higher velocity in an ultra high vacuum (UHV) system to strike against a heated and rotating substrate resulting in condensation of the species on a relatively lower-temperature substrate without any contamination. Usually, Si MBE is performed under UHV conditions for eliminating the unwanted contaminant species as far as it is possible. Because of several stringent conditions to be met, it took quite some time to develop commercial MBE reactors particularly suited to the mass scale production of epitaxial wafers. Although, the process has comparatively lower throughput and is cost intensive due to essential requirement of UHV environment inside the deposition chamber. The MBE process, however, does have a number of inherent advantages over conventional CVD techniques in meeting the precise structures for fabricating over layers for advanced semiconductor devices [2,8].

In yet another variant called liquid phase epitaxial (LPE) growth of semiconductor thin films, the substrate is brought into contact with a saturated solution of the semiconducting material to be deposited at an appropriate temperature. Withdrawal of the dipped substrate resulting in substrate cooling at a suitable rate could allow growing monocrystalline films as observed in case of compounds and III-V alloy semiconductors. Though, LPE could cost much less in producing layers with low defect density and very precise control of stoichiometry, the process suffered from being applicable only in case of a restrictive list of materials besides being difficult to control the morphology with poor surface quality [2,8].

Atomic layer epitaxy (ALE), also called atomic layer deposition (ALD), is another recently developed novel epitaxial deposition process in which the alternate monolayers of two/more elements are deposited onto an underlying substrate in vacuum in a self-limiting mode. The crystal lattice structure achieved in this process is uniform, and aligned with the lattice structure of the underlying substrate. The reactants are brought to the substrate in the form of alternate pulses with a suitable time-gap in between. In ALD, the incoming material species bond strongly until all the sites available for chemisorption are occupied. The time-gap between the two subsequent steps is used to flush out the unreacted materials present there. It is mostly used in semiconductor fabrication to grow thin films of thickness of the atomic order [2,3,8].

After going through these developments that took place in the area of epitaxial growth of semiconductor thin films for device applications, one common point that is noted is the presence of heated substrate that allows the energetic species arriving from their respective sources to travel across the substrate surface leading to their attachment at the appropriately preferred sites leading to 2-D growth of the epitaxial thin film. Every precaution is, however, taken to suppress three-dimensional growth by controlling the operating conditions besides avoiding the entrapment of unwanted species in the deposited layer. Intentionally reducing the operating temperature for minimizing the changes in the doping profiles present there in the underlying substrate caused by the high temperature used, various alternate techniques involving reduced pressure, plasma, and laser assisted depositions have also been explored with success to some extent meeting the additional cost of the required reactor designs. However, the situation of self-limited growth of one monolayer in ALD is practically an ideal situation of preparing precisely controlled thin films for device applications and this capability has extensively been exploited in depositing a large variety of crystalline and noncrystalline thin films at industrial scales [8].

Furthering the concept of depositing monolayers of crystalline materials at the extreme end of this approach, it is natural to ask whether it would be possible to explore a similar process using electrochemical deposition like conditions to grow monolayers of the ionic/neutral species arriving onto the substrate having appropriate surface conditions to bind them. In case, it is feasible to have a situation along these lines, it will definitely be another analog of ALD assisted by the electrochemical excitation of the species in depositing such monolayers in a surface controlled self-limiting manner. For exploring this novel idea, surface reactions taking place in an electrolyte and a potentiostat like set up was employed in recent studies for finding out the answers of various questions before saying confidently that – yes, electrochemical atomic layer deposition (EC-ALD) is a viable option. Various aspects of this

process have been examined in this paper with a view to foresee whether it could take a shape similar to ALD for device fabrication in the times to come affordably [9]. Especially, super lattice based approach of realizing engineered materials with precisely controlled transport properties of electrons and holes derived from EC-ALD would be put to numerous applications in a much better cost-effective way compared to their counterpart attempted using conventional techniques of MBE and ALD at much higher cost [10].

The Electrochemical Processes

Starting from the conventional electroless to electrodeposition of metal thin films, and extending the same to EC-ALD at the extreme end, all the processes involved are electrochemical in nature. The control of the ionic transport in a suitable electrolyte that supplies the required ionic species leading to their deposition on the working electrode must be examined in detail so that out of several possibilities only the one that is required for the specific deposition is rightly found out. This kind of study of developing theoretical models and their experimental validations was carried out in detail in the recent past. Some of those results are presented in the followings to highlight the importance of the processes necessary for atomic level controls of deposition and etching the involved atomically thin monolayers in a systematic manner.

Electrodeposition Process – An Overview

Before going into the details of EC-ALD as the main theme of the discussion in this presentation, it is considered necessary to quickly look into the origin of electroless and electrodeposition processes as studied and used since long. A brief overview is therefore included in the followings.

The phenomenon of electroless metal depositions on a substrate (i.e. metal and other) preceded the well-known process of electrodeposition/electrochemical deposition or commonly known electroplating used in the published literature. The electroless deposition was noted to occur without involving any current flow whereas the process of electrodeposition is accomplished by passing current between two electrodes placed in an electrochemical cell containing a suitable electrolyte. For instance, the decorative gold coatings were formed by electroless gold plating onto a Cu surface exposed to the right kind of electrolyte. The electrons participating in these electrochemical reactions are supplied by the reducing agents present there. The electrodeposition has also been extremely simple to use in applying protective and decorative coatings to metal components in different industrial applications on commercial scales. The development of appropriate electrolytes for silver and gold electrodepositions started appearing as early as around 1840. However, extremely hazardous nature of these electrolytes (e.g. involving mostly cyanides) led to continuing search for safer and better substitutes. This was subsequently followed by exploring environmentally friendly methods against the established electrodeposition processes. Looking at the growing Industrial demands of electrodeposition, the Electrodeposition Division of The Electrochemical Society (ECS) initiated a symposium series called 'Green Electrodeposition'. In parallel with developing new processes, considerable efforts were also made in improving the understanding of the deposition phenomenon as a whole. Establishing a linear relationship between overpotential and the logarithm of the deposition current in 1905 (i.e. explained by statistical thermodynamics) turned out to be a major breakthrough in this context. The influence of screw dislocations in growing electrodeposited metals was studied in the 1960s by conducting the associated experiments resulting in monocrystalline silver crystals. Despite these improved understandings of the related processes, the experimental investigations were not amenable to control at atoimic level for long in the absence of *in-situ* characterization methods of the deposited films in an electrolyte. Attempts were, therefore subsequently, made to examine the involved electrode surfaces after taking them out of the electrolyte for the assessment of the changes occurred during different stages of the depositions. Considerable improvements in characterization results took place after the synchrotron X-ray diffraction and scanning tunneling microscopy (STM) were added to the standard surface characterization methods. The researchers could thus study the electrode surfaces better while still inside the electrochemical cell and this led to accelerated developments thereafter. Using STM could produce images of the electrode surfaces with the details of the atomic positions in addition to manipulating them to produce tiny atomic clusters at predetermined locations. Besides wider applications of electrodeposition in decorative/protective coatings, development of thin films provided enough impetus in realizing magnetic recording heads (hard disks), and replacing aluminum/alloys by electrodeposited copper for interconnects in ultralarge scale integrated circuits [11].

With the advent of nanotechnoloy in the last few decades, the conformal coating of thin films on nanostructured species by electrodeposition was extended for their surface modification/functionalization type of applications. Components like nanowires comprising of few nm thin alternating magnetic and non-magnetic layers and single-electron transistors using niobium are worth mentionig examples in this context. Electrodeposition being a room temperature low-energy process has been well suited for modifying the soft matter of various types. When combined with self-assembled templates nanomaterials could be prepared with exciting properties for their fast emerging applications in the areas like nanoelectronics, biotechnology, and energy engineering [12].

A typical electrodeposition setup contains three electrodes, namely working, reference, and counter electrodes. The electrodes are connected to a potentiostat, which controls the deposition/etching processs. The electrodes are dipped in the electrolyte containing suitable ionic species in a vessel. The working electrode is the one to be plated on; the counter electrode completes the electronic circuit, whereas the reference electrode is used as reference for making the potentiostat. After applying electric field across the working electrode, the electrons entering the solution meet the existing ions resulting in neutral species or compounds that adhere to the working electrode than remaining dissolved in the solution. The applied potential is measured with respect to the reference electrode, however, the current flows in between the working and counter electrodes [13-19].

Metal electrodeposition on foreign substrates involve adsorption of the species available leading to 2D/3D nucleation and growth processes as a function of binding energy between the metal adatoms and substrate and crystallographic misfit between the 3D metal bulk lattice parameters and the substrate. When the binding energy between the depositing metal adatoms and the substrate atoms exceeds that between the atoms of the deposited metal, low dimensional metal phases (0, 1 and 2) are formed onto the foreign metal substrate. This phenomenon of underpotential deposition

(upd) has been studied in the past several decades since the 1970s. Monolayer deposition of metal adatoms under upd is found capable of altering the electronic properties of the substrate material itself by changing the interfacial reactivity. Subsequently, these systems have been the subject of a large number of studies, not only in terms of their fundamental aspects related to electrochemical phenomena (adsorption, charge transfer, nucleation and growth) but also in their technological applications for corrosion inhibition or as models for the design of new electrocatalysts, among many others.

Many electrochemical and surface characterization methods have been employed to study the upd phenomenon. Whereas electrochemical techniques provide valuable information on the kinetics and mechanisms of processes occurring at the metal/solution interface, the molecular specificity required to give unequivocal identification of the species formed at the electrode surfaces are obtained by a number of *in* and *ex-situ* spectroscopies. These methods have been applied to augment electrochemical approaches and provide information on the elemental and molecular composition, the atomic geometry, and the electronic structure of the interface. The great progress that has been made in the development of new *in-situ* techniques allowed to obtain important information on electrode processes at the atomic level.

Cyclic voltammetry (CV) is the useful method of characterizing the upd of a metal adatom on a foreign metal substrate. This consists of a linear scanning of the potential of a stationary working electrode with a constant scan-rate between two chosen limits, one or more times with the continuous monitoring of the current flow. The observed resultant cyclic current-potential curves show location of the redox potentials of electroactive species providing an indication of the effect of media upon the redox processes ging on there. Any reaction at the electrode surface will usually be detected as a current superimposed to the base current due to double-layer charging. The upd process is reflected in cathodic and anodic current density peaks at different potentials, indicating the deposition and dissolution of the metal adsorbate species, respectively. The occurrence of distinct adsorption peaks in the cyclic voltammetric measurements indicates that the formation of 1–2 monolayers at underpotentials taking place in several energetically different adsorption steps. The peak structure is found to depend strongly on the crystallographic orientation of the substrate and the density of crystals imperfections. The number of these peaks and positions also depend on the substrate and the crystal plane on which the adsorption takes place as well as on the nature of the electrolyte. The peaks are not well-pronounced for polycrystalline electrodes whose surfaces present different crystallographically oriented domains and a high density of crystal imperfections (e.g. steps, kinks, vacancies) as compared with single crystals. Some representative examples illustrating what can be achieved with CV are presented here in the following.

Gold was used as electrode material in fundamental electrochemistry of metal upd. Ag adatoms are good examples to study on gold surface as they present strong metal adatom-substrate interactions with negligible misfit (e.g. the lattice parameters, $d_{0,Au}$=0.28840nm, $d_{0,Ag}$ = 0.28895nm). The cyclic-volta-mmograms for Ag upd in the systems Au(100)/Ag+, SO42- and Au(111)/Ag^+,SO_4^{2-} contain three and two adsorption-desorption peaks in the potential range of 15-720mV, respectively. It was demonstrated that potential-cycling in the upd region introduced some surface defects that gradually transformed the surface into a surface alloy phase, leading to the appearance of another Ag upd peak located at 80mV more positive than the first upd peak associated with the deposition of Ag on Au terraces [20].

The ALD Process

Before taking up the description of EC-ALD it will be better to have a quick review of the process of atomic layer deposition (ALD) for understanding the possible extension of electrochemical deposition to 2d-thin films of metals, elemental and compound semiconductors.

In ALD, a thin film is deposited onto a substrate by exposing its surface to alternate gaseous precursors. In contrast to CVD, out of the two precursors involved only one of them is present at a time in the reactor. This is accomplished by involving a series of sequential, non-overlapping pulses. In each of these pulses, the precursor molecules react with the surface in a self-limiting way, so that the reaction terminates once all the reactive sites on the surface are covered. Consequently, the maximum amount of material deposited on the surface after a single exposure to all of the precursors is determined by the nature of the precursor-surface interaction. By varying the number of cycles it is possible to grow materials uniformly and with high precision on arbitrarily complex and large substrates. ALD has great potential for producing very thin, conformal films with atomic level control of the thickness and composition. A major push came from device scaling of microelectronics devices from time to time.

ALD was developed in form of two independent processes named as atomic layer epitaxy (ALE) and molecular layering (ML) from Finland and Soviet Union [21-23]. A substrate is exposed in ALD to two reactants A and B in a sequential, non-overlapping way. In contrast to other techniques such as CVD, where thin film growth proceeds on a steady-state fashion, in ALD each reactant reacts with the surface in a self-limiting manner: the reactant molecules can react only with a finite number of reactive sites on the surface. Once all those sites have been consumed, the growth stops. The unused reactant molecules are flushed away and only then reactant B is inserted into the reactor. By alternating exposures of A and B, a thin film is deposited. Consequently, when describing an ALD process one refers to both dosing and purging times for each precursor. The dose-purge-dose-purge sequence of a binary process constitutes an ALD cycle. ALD processes are described in terms of their growth per cycle. In ALD, enough time must be allowed in each reaction step so that a full adsorption density could be arrived at leading to saturation. This time will depend on two key factors: the precursor pressure, and the sticking probability.

A characteristic parameter of ALD is the sticking probability that changes with time, as more molecules reacting with the surface make this sticking probability reduce until zero value once saturation is arrived at. The specific detail of ALD process depends on the reaction mechanisms used. With hundreds of the processes developed for depositing a large variety of thin films of oxides, metals, nitrides, sulfides, chalcogenides, and fluorides, the unraveling of the mechanistic aspects of ALD processes is an active field of research [22-26].

Another thin film deposition process known as molecular layer epitaxy (MLE) was introduced in Japan while growing compound/ elemental semiconductors using gaseous precursors and heated substrates [27].

Being analogous to conventional vapor phase ALD, it is natural that almost all queries related to the epitaxial deposition including the possibility of controlling electrochemical formation of compound semiconductors necessary for device structure realization, types of electrochemical reactions that initiate ALD cycle, the influence of substrate used or the deposition parameters employed, and the possibility of depositing ternary compounds or graded layer depositions for their use as buffer layers to take care of lattice mismatches, all of them must be addressed to during their detailed investigations. While examining the possibilities of using these thin films in device fabrication, whether it would be possible to dope them to produce n and p-type layers required for junction formation.

The upd Model

The overall structure and physico-chemical properties of EC-ALD deposited thin film onto a substrate have currently been examined using *in-situ*/*ex-situ* characterization techniques. While carrying out numerous theoretical modeling and their experimental validations in the past could suggest that the initial conditions of adsorption/deposition of the adatoms followed by nucleation and growth were essentially responsible for the resultant surface structures and the associated properties. Moreover, such metal/semiconductor adsorbates having sub-monolayer coverage are known possessing significantly different properties compared to their bulk counterpart. Even the adsorbate layers have been noted altering the substrate electronic properties explored for catalysis like applications [28].

In this context, bonding between the adatoms and the substrate was used in controlling the growth as a function of surface coverage during adsorption/deposition of metal adatoms on different metal substrates based on the above model. Further extension of this concept was made in upd of metals resulting in electrodeposition of metal monolayer(s) on a different metallic substrate at potentials that were less negative than that for deposition on the same metal. Better understanding of this phenomena could provide precise and reproducible control of the surface coverage while examining the coverage dependent properties including the structure of the metallic adlayer and its electronic properties. Early upd studies were carried out mostly on polycrystalline electrodes due to the nonavailability of clean monocrystalline substrates of well-defined surface structures. Even though extensive observations were collected from numerous studies; these *ex-situ* measured results became less reliable particularly in case of weakly adsorbed species. With the development of improved procedures and protocols for preparing and cleaning of monocrystalline substrates could introduce great changes in this field of electrodeposition. Precise control of surface coverage and the structures involving single-crystal substrates allowed to address to the problems of interfacial reactivity including corrosion, electrocatalysis, and likewise. While controlling and measuring the thermodynamic parameters like potential, charge, and coverage in this process, the structural details derived from *ex-situ* measurements were only of indirect nature. The availability of *in-situ* characterization techniques eliminated much of these uncertainties involved and consequently generated ample interest in case of single-crystal surfaces. Such advanced *in-situ* techniques could characterize these growing thin films under active electrochemical control. Applications of FT-IR, Raman, and second harmonic generation (SHG) along with *in-situ* measurement by grazing incidence X-ray scattering, surface SEXAFS, and X-ray standing waves and scanned probe microcopies (STM, AFM, and related methods), further improved the quality assessment of surfaces and their structurea up to atomic levels. An exhaustive review, published sometime back, examined the phenomena of metal upd in mono and multilayer forms on single crystal electrode surfaces. Some of the observations made there are summarized here in the following [28, 29].

The structural details of the electrodeposited metal monolayers onto well-ordered single-crystal electrode surfaces were examined in case of gold, platinum, and silver substrates. The electrodeposition was realized with well-defined surface structures at sub and full-monolayer coverage. The kinetics of electrodeposition/desorption as well as the resulting structures were noted to depend on the nature and concentration of anions. In the presence of the weakly adsorbing anions like perchlorate, the deposition/desorption kinetics were noted to be slow. The presence of strongly interacting anions like halides (excluding fluoride) demonstrated much faster kinetics often resulting in coadsorbed layers. The formation of these layers were associated in some cases with phase transitions. Commensurate and incommensurate structures were noted in presence of small and large lattice mismatches between the adsorbate and the substrate, respectively. A general mechanism for the monolayer formation was thus found possible involving a sequence of electrodeposition of the metal atoms coupled with the coadsorption of anions to form a 2-D metal anion layer. Further reductions could disrupt these layers with additional electrodeposition leading to the formation of a zero valent metal adlayer. The enhanced reactivity sites created along the steps greatly modified the structures and kinetics having preferred adsorption of both metal and anions [28].

The overall structure and physico-chemical properties of EC-ALD deposited thin film onto a substrate have currently been examined using *in-situ*/*ex-situ* characterization techniques. Theoretical studies and their experimental confirmations carried out in the past could suggest that the initial conditions of adsorption/deposition of the adatoms followed by nucleation and growth were essentially responsible for the resultant surface structures and the associated properties. Moreover, such metal/semiconductor adsorbates having sub-monolayer coverage are known possessing significantly different properties compared to their bulk counterpart.

In this context, the nature of bonding between the adatoms and the substrate was used in controlling the growth as a function of surface coverage during adsorption/deposition of metal adatoms on different metal substrates. Further extension of this concept was made in upd of metals resulting in electrodeposition of metal monolayer(s) on a different metallic substrate. Better understanding of this phenomena could provide precise and reproducible control of the surface coverage while examining the coverage dependent properties including the structure of the metallic adlayer and its electronic properties. With the development of improved procedures and protocols for preparing and cleaning of monocrystalline substrates could introduce better models of electrodeposition.

For understanding the process of electrodeposition of epitaxial compound semiconductors of the required quality necessary for fabricating electronic and optoelectronic devices, experimental and theoretical studies have been carried out in detail in electrochemical atomic layer deposition during last two decades. This process being of surface limited reaction type has been found forming one monolayer of material at a time quite analogous to conventional vapor phase ALD. This type of material growth employs upd.. The driving

force involved in EC-ALD is indeed the free energy of compound formation at the surface. An atomic layer of each element is deposited in turn, in a cycle, to form a monolayer of the compound, and thus the number of cycles determines the thickness of the deposited thin film. The EC-ALD breaks the process of stoichiometric compound electro-deposition into a series of fundamental steps, allowing for their independent controls and characterizations required for further understanding of the processes involved.

Each element of in EC-ALD has its own upd-chemistry, which must be studied thoroughly to decide about the parameters of a deposition cycle. This cycle is essentially the chosen sequence of steps used in depositing the required stoichiometric of the desired material. This could be an atomic layer for a pure element, or a bi-layer of a 1:1 compound. For example, in CdS EC-ALD cycle, it involves depositing an atomic layer of S onto that of Cd, and similarly, one of Cd onto that of S. This EC-ALD cycle is composed of four steps - oxidative sulfur-upd forming S^{2}- ion solution, a blank rinse, reducing Cd-upd from a Cd^{2+} ion solution, followed by a second blank rinse. Different solutions are used for each reactant as well as different potentials for each step of the deposition cycle. Thus, using separate solutions and potentials offers an extensive control over deposit growth, composition, and morphology. A cycle may be repeated to form a nano film, with the deposit thickness being a linear function of the number of deposition cycles. This linear growth is an indication of a layer-by-layer deposition of an ALD process. There are a number of cycle chemistries that can be applied, depending on the elements involved. For instance, the CdS deposition cycle involves an oxidative-reductive upd-cycle (O-R). There are few compounds formed using O-R sequence, because of a lack of suitable negative oxidation state precursors (like S^{2+}), for which oxidative upd is practicable. Other cycle chemistries include reductive-reductive upd (R-R), R-R with a reductive strip (R-R-R), R-R with an oxidative strip (R-R-O), bait and switch (B/S), and surface limited redox replacement (SLRR) [29].

In an automated flow-deposition EC-ALD system, a computer manipulates the required changes in the potential applied and the solutions used precisely as a function of time. The *in-situ* characterization of the deposited layers are carried out using electrochemical scanning tunneling microscopy (ECSTM), electrochemical quartz crystal microbalance (EQCM), ultrahigh vacuum electrochemistry (UHV-EC) as well as reflection, absorption, luminescence, photo-electrochemical, photoconductivity, and Hall measurements for studying their physical and electronic properties.

Particularly, the operating temperature in EC-ALD is quite a significant parameter as compared to various vacuum and gas based deposition systems as mentioned already. Most importantly, the EC-ALD process is carried out at room temperature or at the most under the boiling point of the solvent. All these temperatures are fairly low for thin film depositions. Besides, these deposits are prepared under equilibrium conditions where in the potential is applied until the current reduces to zero while composition and structure remain unchanged. However, the electrochemical deposition is a dynamic process under dynamic equilibrium of deposition and dissolution occurring simultaneously. The measured current is the difference between the deposition and dissolution flux, and when it is zero, the equilibrium condition is established. The current is a measure of the rate at which atoms are depositing and dissolving, at equilibrium. Ideally, atoms in high-energy sites are dissolving and re-depositing in more stable sites. The result is similar to thermal annealing, or to surface diffusion, in gas or vacuum phase thin film depositions [29].

The EC-ALD reactor is an electrochemical cell that has provisions for the rapid exchange of solutions used in the process in a precisely controlled manner. The manual system is rather slow and prone to error than the one controlled automatically using computer. The deposition-cycles can be programmed, and made to run for as many cycles as required in precisely controlled way. Thus, it requires as many solution lines as the number of elements required depositing the target structure. More complex sequences of potentials and solution exchanges have been performed as well, such as the formation of a super-lattice, where two or more materials are deposited alternately to form materials with unique lattice constants, and optical and electronic properties [29].

Experimental Results

The experimental results reported in current publications indicate sufficient proof of the maturity of the deposition process for its device applications. Some of the representative results are included in the followings to validate the theoretical predictions made by researchers from time to time.

Experimental Validations

Epitaxial CdTe, CdSe, and CdS thin films were electrodeposited by EC-ALD, using an automated electrochemical deposition system resulting in improved quality and reproducibility of these depositions as checked using electron probe microanalysis, scanning electron microscopy, and grazing incident diffraction experiments. These results confirmed the layer-by-layer growth mode of atomic layer epitaxy. CdTe films were grown up to 1000 EC-ALD cycles. Probably due to less than ideal deposition parameters used the deposited layers were found stoichiometric through 500 cycles whereas the 1000 cycle films were found to be a few percent rich in Te content. CdSe and CdS films also contained some excess chalcogenide. Increasing amounts of the particulates and surface roughening were observed for the 500 and 1000 cycle CdTe and CdSe films, relative to the 200 cycle deposits normally formed [30].

Electrochemical deposition processes for fabricating devices including photo electro chemical devices, batteries, fuel cells, and super capacitors are showing better promises for onsite energy harvesting. While developing materials with the desired properties, especially the quality of various interfaces involved is, in general, found critical for the performance of these devices. ALD is most appropriate tool for precise engineering of material properties on atomic scale as reviewed recently by focusing on the current status of the applications, perspective and challenges of atomic layer deposition process on the electrochemical energy generation and storage devices and processes [31].

Combining the phenomenon of semiconductor solvation in liquid metal with the simplicity of a conventional electro-deposition, a new electro chemical deposition methodology was reported for direct growth of crystalline covalent group IV and III–V semiconductor materials at or near ambient temperature conditions. This process was termed as electrochemical liquid–liquid–solid (ec-LLS) crystal growth involving low-temperature liquid metal (i.e., Hg, Ga, or alloy thereof) to simultaneously act as the source of electrons for the heterogeneous reduction of oxidized semiconductor precursors dissolved in an electrolyte and the solvent for dissolution of the

zero-valent semiconductor. Super-saturation of the semiconductor in the liquid metal is used to initiate nucleation and crystal growth of the layer under consideration. In this way, the boundaries at the liquid electrolyte–liquid metal–solid (ec-LLS) crystal phase could strongly influences crystal growth. The ec-LLS growth is carried out at room temperature without involving toxic precursors, or high-energy-intensive chemical processes. This simplifies the equipment design further and the fabrication costs. It is possible to carry out ec-LLS experiment in a beaker filled with electrolyte and an electrical circuit capable of supplying the defined current. Furthermore, the process of ec-LLS is even applicable with thermally and chemically sensitive substrates like plastics that cannot be used as deposition substrates in conventional syntheses of covalent semiconductors. Layer grown using ec-LLS growth affords control over a host of crystal shapes and sizes through simple changes in common experimental parameters. Large and small semiconductor crystals are grown both homogeneously within a liquid metal electrode and heterogeneously at the interface of a liquid metal electrode and a seed substrate, depending on the particular details chosen for ec-LLS. Further, the rate of introduction of zero-valent materials into the liquid metal is precisely gated with a high degree of resolution by the applied potential/current. The key elements of ec-LLS process were identified with respect to other semiconductor crystal growth methods by highlighting the unique capabilities of ec-LLS. Specifically, using ec-LLS as a platform for depositing Ge and Si crystals from bulk- ($1cm^3$), micro ($10^{-10}cm^3$), and nano-sized ($10^{-16}cm^3$) liquid metal electrodes in common solvents at low temperature. In addition, the success achieved was demonstrated in preparing more compositionally complex binary III–V semiconductors.

In a novel process of ec-LLS one could produce monocrystalline silicon @ 80°C without any physical or chemical template as demonstrated via electro-reduction of dissolved SiCl4 in propylene carbonate with a liquid gallium as working electrode. This yielded crystalline Si as confirmed by X-ray and electron diffraction data separately indicating that the as-deposited materials were crystalline with the expected patterns for a diamond cubic crystal structure. Scanning and transmission electron microscopies revealed the as-deposited materials to be faceted nano crystals with diameters in excess of ~500 nm. Energy-dispersive X-ray spectra further showed no evidence of any other species within the electrodeposited crystalline Si. Raman spectral analyses separately showed that the electrodeposited films on the electrodes were not composed of amorphous carbon from solvent decomposition. These results confirmed that liquid-metal electrode could serve simultaneously both as a source of electrons for the heterogeneous reduction of dissolved Si precursor in the electrolyte and a separate phase that promoted Si crystal growth. Thus, ec-LLS process could be used for direct production of crystalline Si at much lower temperatures than ever reported previously [33].

Direct epitaxial growth of single-crystalline germanium (Ge) nanowires at room temperature was prepared using an electro-deposition process on conducting wafers immersed in an aqueous bath. The crystal growth was based on an electrochemical liquid–liquid–solid (ec-LLS) process involving the electro-reduction of dissolved GeO2 in water at isolated liquid gallium nano droplet electrodes resting on single-crystalline Ge or Si supports. Ge NWs were electrodeposited on the wafer scale (>10cm2) using simple glassware and a digital potentiostat. High-resolution electron micrographs and electron diffraction patterns collected from the cross sections of the individual substrate-nanowire contacts in addition to SEM of the orientation of the NWs across entire films on substrates with different crystalline orientations supported the epitaxial nature of the growth. Energy dispersive spectroscopic elemental mapping of single nanowires indicated the Ga(l) nano droplet remaining affixed to the tip of the growing NW throughout the electro-deposition process. Current–voltage responses measured across many individual nanowires yielded reproducible resistance values. The presented data cumulatively show epitaxial growth of covalent group IV nanowires is possible from the reduction of a dissolved oxide under purely bench-top conditions [34].

Highly ordered crystalline Ge micro wire arrays with individual diameters larger than 1μm have been grown in aqueous solutions at ambient pressure and below the boiling point of water through ec-LLS crystal growth process. A pertinent feature of this work was the use of a liquid metal patterning strategy, which combined the utility of photolithography with the simplicity of doctor blading to produce macroscopic (>$1cm^2$) arrays of liquid metal microelectrodes. Optical and SEM showed the compatibility of the liquid metal patterning process and subsequent ec-LLS micro wire growth with a wide assortment of different conducting substrates, including silicon, indium tin oxide, copper foil, titanium foil, stainless steel, and poly [(3,4-ethylenedioxy) thiophene]/poly (styrene sulfonate). Furthermore, a simple chemical bath lift-off procedure was developed to fully remove the Ge micro wire arrays embedded in SU-8 photoresist without perturbing the order or quality of the material, resulting in a free-standing composite membrane. Data from energy-dispersive spectroscopy, Auger nano probe spectroscopic mapping, and four-terminal single micro wire electrical measurements indicated that the specific liquid metal used for ec-LLS impacted the morphology and electrical properties of the resultant Ge micro wires [35].

Transistors were already been fabricated tri gate field-effect transistor (FinFET) configuration with taller, thinner, and closer geometries together to enhance device performance and lower active power consumption. With the device scaling, these transistors would require more advanced, fabrication-enabling technologies for the conformal deposition of high-κ dielectric layers on their 3D channels with accurate alignment and thickness control down to the sub-nanometer scale. Among many competing techniques, area-selective atomic layer deposition (AS-ALD) is a promising method that was noted to be well suited to the requirements without the use of complicated, complementary metal-oxide semiconductor (CMOS)-incompatible processes. However, further progress was limited by poor area selectivity for thicker films formed *via* a higher number of ALD cycles as well as the prolonged processing time. A self-correcting ALD approach, combining selective deposition with a post-process mild chemical etching, which enabled selective deposition of dielectric films with thicknesses and processing times at least 10 times larger, and 48 times shorter, respectively, than those obtained by conventional AS-ALD processes. These advances offered a technological breakthrough to drive the AS-ALD technique a step closer toward industrial applications in electronics, catalysis, and photonics with more efficient device fabrication processes [36].

Co_3O_4 nano layers were successfully deposited on a flexible carbon nanotubes/carbon cloth (CC) substrate by atomic layer deposition. Much-improved capacitance and ultra-long cycling life was achieved

when the CNTs@Co_3O_4/CC was tested as a super capacitor electrode. The improvement could be affected from the mechanically robust CC/CNTs substrate, the uniform coated high capacitance materials of Co_3O_4 nanoparticles, and the unique hierarchical structure. The flexible electrode of CNTs@Co_3O_4/CC with high areal capacitance and excellent cycling ability promised the great potential for developing high-performance flexible super capacitors [37].

The electrochemical liquid−liquid−solid deposition of crystalline Ge in a eutectic mixture of liquid gallium and indium was analyzed as a function of liquid metal thickness, process temperature, and flux. Thicknesses ≤8μm consistently facilitated heterogeneous nucleation of Ge at the underlying solid support. The required super-saturation was approximately 10^2 larger than the equilibrium concentration of Ge in e-GaIn [38].

In2Se3, thin films were room temperature electrodeposited from an aqueous solution containing ionic precursors for both In and Se, using potential pulse atomic layer deposition (PP-ALD). Cyclic voltammetry was used to determine approximate cycle potentials, and anodic and cathodic potentials were systematically examined to optimize the potential pulse program for In_2Se_3. Electron probe microanalysis was used to follow the In: Se atomic ratio as a function of the cycle conditions, and annealing studies were performed on stoichiometric deposits. Film thickness was noted as a function of both the anodic and cathodic potentials. The optimum growth rate was consistent with previous PP-ALD studies in which similar concentrations and pulse times were employed, 0.02 nm/cycle. The use of the potential pulse cycle for film growth resulted in surface-limited control over the deposit stoichiometry each cycle and thus a layer-by-layer growth process [39].

Crystalline thin films of cuprous selenide (Cu_2Se) were electrodeposited at room temperature from an aqueous solution containing elemental precursors for Cu and Se, using a potential pulse version of atomic layer deposition. CV was used to estimate anodic and cathodic cycle potentials for the formation of Cu_2Se, which were then examined to systematically optimize the cycle. EPMA was used to follow the Cu/Se atomic ratios as a function of the cycle parameters, and X-ray diffraction was used to investigate deposit the structure: polycrystalline orthorhombic Cu_2Se, with some cubic phase. Film thicknesses, from spectroscopic ellipsometry, were shown to be proportional to the number of cycles performed (0.02 nm/cycle), and scanning electron microscopy suggested that the deposits were consistent with layer-by-layer growth as a function of the number of cycles [40].

Area selective atomic layer deposition has the potential to significantly improve current fabrication approaches by introducing a bottom-up process in which robust and conformal thin films are selectively deposited onto patterned substrates. A selective deposition of dielectrics was presented on metal/dielectric patterns by protecting metal surfaces using alkanethiol-blocking layers. Alkanethiol self-assembled monolayers (SAMs) with two different chain lengths were deposited both in vapor and in solution phases. From these, it was shown that the thiols have the ability to block surfaces against dielectric deposition. It was further noted that thiol molecules could displace Cu oxide, opening possibilities for easier sample preparation. A vapor-deposited alkanethiol SAM was shown to be more effective than a solution-deposited SAM in blocking ALD, even after only 30s of exposure. The vapor deposition also resulted in a much better thiol-regeneration process facilitating deposition of the SAMs on porous or three-dimensional structures, allowing for the fabrication of next generation electronic devices [41].

Deposition of epitaxial Ge thin films on Si wafers was achieved over large areas with aqueous feedstock solutions using ec-LPE at low temperatures (T ≤ 90°C). This method blended the simplicity and control of traditional electro-deposition with the material quality of melt growth. A new electrochemical cell design based on the compression of a liquid metal electrode into a thin cavity that enabled ec-LPE was demonstrated. Methods like electron backscatter diffraction, scanning transmission electron microscopy, high resolution X-ray diffraction, and electron channeling contrast imaging with low strain character, and crystallographic defect content of the resultant solid Ge films. These results offered the first step toward a manufacturing process for traditional crystalline inorganic semiconductor epitaxial-films that does not require high temperature, gaseous precursors, or complex apparatus [42].

The ec-LLS deposition of crystalline Ge in a eutectic mixture of liquid gallium (Ga) and indium (In) was analyzed as a function of liquid metal thickness, process temperature, and flux. Through control of reaction parameters, conditions were identified that allowed selective nucleation and growth of crystalline Ge at the interface between e-GaIn and a crystalline Si substrate. The crystal growth rates of Ge by ec-LLS as a function of process temperatures were obtained from time-dependent powder X-ray diffraction measurements of crystalline Ge. The driving force, for crystal formation in ec-LLS was estimated through analyses of the experimental data in conjunction with predictions from a finite-difference model. The required force for Ge nucleation was found closer to the super-saturation - approximately 102 times larger than the equilibrium concentration of Ge in e-GaIn at the investigated temperatures [43].

In one of the attempts of developing a bottom-up synthesis of inorganic III-V 3D-nanostructures for fabricating low cost energy conversion devices involving confined electrochemical deposition through a scanning probe nano electrode. For a rapid deposition of usable nanostructures, the application tool for nano electrochemical growth was developed with atomic force microscopes. This platform offered new possibilities to current additive nano manufacturing tools with the potential to fabricate one sheet after the other by using multi-electrode arrays. The flexibility and low-cost of the fabrication method could be used for generating novel devices, particularly in the domain of photonics and energy conversion [44].

Area-selective atomic layer deposition is rapidly gaining popularity because of its potential application in self-aligned fabrication schemes for next-generation nano electronics. An approach of area-selective ALD was described in a recent publication that relied on the use of chemo-selective inhibitor molecules in a three-step (ABC-type) ALD cycle. A process for area-selective ALD of SiO_2 was developed comprising acetylacetone inhibitor (step A), bis (diethylamino) silane precursor (step B), and O_2 plasma reactant (step C) pulses. The results observed showed that this process could allow for selective deposition of Si O_2 on GeO_2, SiN_x, SiO_2, and WO_3, in the presence of Al_2O_3, TiO_2, and HfO_2 surfaces. *In-situ* FTIR spectroscopy and DFT calculations made it clear that the selectivity of the approach came from the chemo-selective adsorption of the inhibitor. The selectivity between different oxide starting surfaces

and the compatibility with plasma-assisted or ozone-based ALD were distinct features of this approach. Furthermore, the approach offered unique opportunity of tuning the substrate-selectivity by proper selection of inhibitor molecules [45].

The thermal chemistry of Cu(I)-sec-butyl-2-iminopyrrolidinate in an experiment of copper amidinate complex for atomic layer deposition applications, was explored comparatively on several surfaces by using a combination of surface-sensitive techniques, specifically temperature-programmed desorption and X-Ray photoelectron spectroscopy (XPS). The substrates explored included single crystals of transition metals (Ni (110) and Cu (110)), thin oxide films (NiO/Ni (110) and SiO_2/Ta), and oxygen-treated metals (O/Cu (110)). Decomposition of the pyrrolidinate ligands led to desorption of several gas-phase products, including CH_3CN, HCN and butene from the metals and CO and CO_2 from the oxygen-containing surfaces. The dehydrogenation of the organic moieties was accompanied by hydrogen removal from the surface, in the form of H2 on metals and mainly as water from the metal oxides. The threshold for this chemistry varied wildly, from 270K on Ni (110) to 430K on O/Cu (110), 470 K on Cu (110), 500K on NiO/Ni (110), and 570 K on SiO_2/Ta. Copper reduction was also observed in both the Cu 2p3/2 XPS and the Cu L3 VV Auger (AES) spectra, reaching completion by 300 K on Ni (110) but occurring only between 500 and 600K on Cu (110). On NiO/Ni (110), both Cu (I) and Cu(0) coexisted between 200 and 500K, and on SiO2/Ta a change happens between 500 and 600K but the reduction was limited, with the copper atoms retaining a significant ionic character. Additional experiments could test adsorption at higher temperatures leading to the identification of temperature windows for the self-limiting precursor uptake required for ALD between approximately 300 and 450K on both Ni (110) and NiO/Ni (110); the range on SiO_2 had been previously determined to be wider, reaching an upper limit at about 500K. Finally, deposition of the Cu films via ALD cycles with O_2 as the co-reactant was successfully accomplished on the Ni (110) substrate [46].

The application of surface limited redox replacement (SLRR) protocol was described for EC-ALD of Pd ultrathin films on Au in a single cell using under-potentially deposited H (H_{UPD}) as the sacrificial mediator. The facile deposition approach presented required neither the use of sophisticated instrumentation nor the presence of metal ions other than the Pd (II) chloride complex. This provided for maximum growth efficiency and eliminated potential contamination of the deposit thereby rendering the Pd deposition a "greener" process. The growth was monitored by open circuit chronopotentiometry while CV of H_{UPD} and Cu_{UPD} helped in assessing the roughness of the Pd films. These results indicated the deposition of smooth Pd films occurring for up to 30 SLRR cycles (20 equivalent monolayers) followed by a rapid transition to dendritic growth at higher thickness. The quasi-2D growth, resulting in smooth and uniform Pd-film morphology was also confirmed up to 20 SLRR cycles by *in-situ* STM. Analysis of the results from Pd-film stripping experiments corroborated these findings. The comparison of charges obtained by the stripping of Pd films of different thickness with growth models suggested that not only adsorbed but also absorbed H_{UPD} participated in redox exchange with $[PdCl_4]^{2}$-complex in 2:1 stoichiometric ratio. The presented approach offered contamination-free Pd deposition with unsurpassed simplicity extended to other conducting substrates featuring strong H-affinity [47].

2D materials are the most useful nanomaterials due to their potentials in next-generation electronics. Because most of the 2D materials are atomically thin, a suitable fabrication process without degradation of the original properties of the material is required to realize 2D-material-based devices. Atomic layer deposition (ALD) is an ideal technique for adding materials with atomic scaling precision to nanomaterials. Due to the surface-sensitive reactions of ALD, growth of 2D materials is strongly affected by the surface properties of the 2D materials. ALD growth on 2D materials was reviewed and discussed in a recent work along with previously reported results to provide insights in this area [48].

The ability to produce or alter materials to obtain drastically different or improved properties has been the target of materials science since its inception. Interdisciplinary approaches involving multiple elements, compounds, or materials with the useful aspects of each constituent has been solved as a complex problem. Hybrid materials incorporating organic and inorganic components are used in a large variety of new materials and techniques to produce them. One of the most recent being combination of atomic layer deposition, which produces inorganic materials, and molecular layer deposition (MLD), which employed organic materials. Hybrid materials through bottom-up combinations of ALD and MLD were reviewed, focusing on the process and properties of the resulting materials. The modification of biomaterials through coating was discussed, and finally the relatively new concept of vapor phase infiltration was considered as a new and unique method to produce hybrid materials from a top down approach [49].

Developing synthetic methods for modifying the physico-chemical properties of nanostructured species has been used in realizing materials by design to have complex architectures. Although, structures based on one-dimensional (1D) Si synthesized using top-down and bottom-up methods are known to be prominent for diverse applications in chemistry, physics, and medicine, yet, further applications of these structures with distinct metal and polymeric bases, have been difficult to explore. A general electrochemical method was reported for depositing conformal layers of various materials onto high aspect ratio Si micro and nanowire arrays. The electrochemical deposition of a library of coaxial layers comprising metals, metal oxides, and organic/inorganic semiconductors demonstrated the generality of this synthesis technique. Depositions were possible on wire arrays with varying diameter (70nm - 4μm), pitch (5μ - 15μ), aspect ratio (4:1- 75:1), shape (cylindrical, conical, hourglass), resistivity (0.001–0.01 to 1–10 ohm/cm^2), and substrate orientation. Anisotropic physical etching of wires with one or more coaxial shells yielding 1D structures with exposed tips could be further site-specifically modified by an electrochemical deposition approach. This electrochemical deposition technique featured as a wafer-scale synthesis platform for the preparation of multifunctional nanoscale devices based on a 1D Si substrate [50].

EC-ALD formation of nano films of materials involving the galvanic exchange of a less noble metal, deposited using upd to produce an atomic layer of a nobler element by reduction of its ions. This process also called surface limited redox replacement could be repeated in a cycle to grow thicker deposits. Previously performed on nanoparticles and planar substrates, EC-ALD was applied for coating a submicron-sized powder substrate, making use of a new flow cell design for coating a Pd-powder substrate with different thicknesses of Rh by exchanging it for Cu upd. Cyclic voltammetry

and X-ray photoelectron spectroscopy indicated an increasing Rh coverage with increasing numbers of deposition cycles performed, in a manner consistent with ALD mechanism. Cyclic voltammetry also indicated increased kinetics of H sorption and desorption in and out of the Pd powder with Rh present, relative to unmodified Pd [51].

Electrodeposition of the first Pd layers onto Pt (100) was investigated using CV at a low scan rate (0.1mV/s). Ultrathin films were characterized in 0.1 M H_2SO_4 solution and with *ex-situ* AFM. For the first time, the under potential character of the deposition of the first two Pd layers was observed characterized by a two-step mechanism, each step corresponding to the deposition of a complete Pd atomic layer. For thicker deposits (especially above 10 monolayers thickness) the electrochemical characterization displayed a strong irreversibility and a broadening of the adsorption/desorption peaks, associated with a reduction of long-range ordered flat areas. *Ex-situ* AFM images were in agreement with this description. They showed rough thick deposits and the growth of (100)-oriented rectangular shaped islands with their sides aligned with the two [011] and [0-11] perpendicular directions of the (100) Pt surface [52].

Hemispherical shell micro-resonators were examined as gyroscopes to enable precision inertial navigation and guidance at low cost and size. Such devices require a high degree of symmetry and large quality factors (Q). Fabricating these devices from atomic layer deposition (ALD) facilitated the required symmetry through ALD's high conformality and low surface roughness. To maximize Q, the shells' geometry was optimized using finite element method (FEM) studies to reduce thermo-elastic dissipation and anchor loss. The shells were fabricated by etching hemispherical molds in Si (111) substrates with a 2:7:1 volume ratio of hydrofluoric: nitric: acetic acids, and conformal coating and patterning the molds with ALD Al_2O_3. The Al_2O_3 shells were then released from the surrounding Si substrate with SF6 plasma. The resulting shells typically had radii around 50 µm and thicknesses close to 50 nm. The shells are highly symmetric, with radial deviations between 0.22 and 0.49%, and robust enough to be driven on resonance at amplitudes 10 × their thickness, sufficient to visualize the resonance mode shapes in an SEM. Resonance frequencies were around 60 kHz, with Q values between 1000 and 2000. This Q is lower than the 10^6 predicted by FEM, implying that Q is being limited by un modeled sources of energy loss, most likely from surface effects or material defects [53].

Ge nano films were deposited in a self-limited mode from aqueous solutions using the electrochemical analog of ALD as a function of solution pH. The EC-ALD cycle involved inducing a Ge atomic layer to deposit on a Te atomic layer formed onto Ge, via upd. The Te atomic layer was then reductively stripped from the deposit, leaving the Ge and completing the cycle. The Te atomic layer was bait for Ge deposition, after which the Te was switched out, reduced to a soluble telluride, leaving the Ge (one “bait and switch” cycle). The deposit thickness was a linear function of the number of cycles. Raman spectra indicated formation of an amorphous Ge film, consistent with the absence of a XRD pattern. Films were more stable and homogeneous when formed on Cu substrates, than on Au, due to larger hydrogen over potential, and the corresponding lower tendency to form bubbles [54].

The effect of UV light during Ge electrodeposition on Au and indium tin oxide (ITO) from the ionic liquid 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) amide was investigated and reported. From CV analysis, two reduction peaks were observed and were assigned to the reduction of Ge (IV) to Ge (II) species, and Ge(II) to Ge(0) species. On using 254nm UV light during electrodeposition, a decrease of 140mV occurred on the ITO substrate for the reduction of Ge (IV) to Ge (II) compared with that observed without UV, and a decrease of 204mV was observed in the reduction of Ge (II) to Ge. The shift in the reduction peak seems to be related to the photo absorption of UV by the electrolyte, possibly altering the ionic liquid/ electrode interface. By characterizing the deposit using SEM, it was noted that the presence of UV irradiation significantly decreased the Ge particle size. A green luminescence was also observed from the electrolyte during the CV experiments in the presence of UV [55].

The electrodeposition of Si_xGe_{1-x} was reported from 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) amide containing different molar concentrations of $SiCl_4$ and $GeCl_4$. Deposition of Si_xGe_{1-x} using a 1:1 molar ratio of $SiCl_4$ and $GeCl_4$ showed a color change of the deposit from red to green during the CV scan. On increasing the concentration of $SiCl_4$, only a reddish deposit was seen. When the concentration of $GeCl_4$ was increased, only a black deposit was obtained. Constant potential electrodeposition showed the formation of Si_xGe_{1-x} with varying proportions of Si to Ge on changing the molar ratio of the solution. To further evaluate the reaction mechanism of the electro-deposition process, *in-situ* UV visible spectro-electro-chemistry was performed. From the changes in the UV spectra combined with XPS and SEM observations, a layered growth process was proposed during the formation of Si_xGe_{1-x} [56].

In-situ UV–visible spectroscopic measurements were carried out during the electrodeposition of Si, Ge, and Si–Ge alloys from an ionic liquid. From the spectroscopic analysis, the potential-dependent formation and growth of Ge, Si, and Si_xGe_{1-x} NPs were evaluated. The possible formation of ad layers and an upd of Si on Ge during Si and Ge electro deposition were also studied in detail [57].

Si electrochemical deposition was carried out in an ionic liquid medium in the presence of water in a limited dry nitrogen environment on highly oriented pyrolytic graphite (HOPG) at room temperature. It was found that the presence of water in ionic liquids did not affect the available effective potential window to a large extent. Si was successfully deposited electrochemically in the over-potential regime in two different ionic liquids, namely, $BMImTf_2N$ and $BMImPF_6$, in the presence of water. Although a Si thin film was obtained from $BMImTf_2N$; only distinguished Si crystals protected in ionic liquid droplets were observed from $BMImPF_6$. The most important observation of the present investigation was that $SiCl_4$, instead of undergoing hydrolysis, even in the presence of water, coexisted with ionic liquids, and elemental Si was successfully electrodeposited [58].

Current Status of EC-ALD

Nanocrystalline Sb_2Te_3 thin film was for the first time reported using EC-ALD after analyzing the electrochemical behavior of Te and Sb on Pt, Te on Sb-covered Pt, and Sb on Te-covered Pt by methods including cyclic voltammetry, anode potentiodynamic scanning, and coulometry. A steady deposition of Sb_2Te_3 was realizd after negatively stepped adjustment of upd potentials of Sb and Te on Pt in each of the first 40 depositing cycles. The structure of the deposited film was XRD analyzed and the stoichiometric composition of Sb and Te (i.e. 2:3) was also confirmed by EDX and coulometry.

Nanocystalline microstructure with average grain size ~20nm was measured in Sb_2Te_3 deposits. Cross-sectional SEM cofirmed 19nm thick layer sandwiched between the Sb_2Te_3 nanocrystalline deposit and the Pt substrate surface. The optical band gap of 0.42eV (FTIR spectroscopy) was assessed for deposited Sb_2Te_3 films [59].

The stoichiometric growth of $CuInSe_2$ (CIS) on Au was reported using EC-ALD by controlling potentials, step sequence, solution compositions and timing. CIS was also grown by combining cycles for two binary compounds, InSe and Cu_2Se, using a super lattice sequence. Stoichiometric samples were formed using the super lattice sequence by performing 25 periods, each consisting of 3 cycles of InSe and 1 cycle of Cu2Se. The deposits were grown using 0.14, −0.7, and −0.65V for Cu, In, and Se precursor solutions, respectively. XRD patterns displayed peaks consistent with the chalcopyrite phase of CIS, for the as-deposited samples, with the (112) reflection as the most prominent. AFM images of the resultant deposits suggested conformal deposition, when compared with corresponding image of the Au on glass substrate [60].

In order to make use of better CO tolerant nature of PtRu catalysts compared to pure Pt and other Pt-based alloys, a bimetallic PtRu nano film was prepared using EC-ALD for fuel cell applications. The metal nano films were prepared involving surface-limited redox replacement (SLRR), where an atomic layer (AL) of a sacrificial metal was first formed by upd. The AL was then spontaneously exchanged for a more noble metal at the open-circuit potential. In this manner, PtRu nano films were prepared using SLRR for Pt and Ru, and Pb UPD was used to form the sacrificial layers. The PtRu EC-ALD cycle employed Pb UPD at −0.19V, followed by replacement using Pt-ions at OCP, rinsing with blank, then Pb UPD at −0.19V, followed by replacement using Ru-ions at OCP. PtRu nano film thickness was controlled by the number of cycles repeated. PtRu nano films with atomic proportions of 70/30, 82/18, and 50/50 Pt/Ru were formed on Au on glass slides using EC-ALD cycles. The charge for Pb upd and changes in the OCP during replacement were controlled during the deposition process. The PtRu films were then characterized by CO adsorption and electro-oxidation to determine their over-potentials. The 50/50 PtRu nano films displayed the lowest CO electro-oxidation over-potentials as well as the highest currents, compared with the other alloy compositions, pure Pt, and pure Ru. In addition, CO electro-oxidation studies of the terminating AL on the 50/50 PtRu nanostructured alloy were investigated by depositing one or two SLRR of Pt, Ru, or PtRu on top [61].

The EC-ALD of Pd thin films was carried out using SLRR of Cu upd on polycrystalline Au substrates. An automated electrochemical flow deposition system was employed for depositing Pd atomic layers using a sequence of steps. Initially, Cu was under-potential deposited, followed by its exchange for Pd ions at open circuit, and finishing with a blank rinse to complete the cycle. Further analyses of the deposits suggested that the SLRR mechanism did not involve direct transfer between Cu_{UPD} atom and a Pd^{2+} ion that would take its position. Instead, it was proposed that electrons were transferred through the metallic surface to reduce Pd^{2+} ions near the surface where their activity is highest [62].

In another application of SLRR protocol used for EC-ALD of Pd films on Au in a single cell using HUPD as the sacrificial mediator. This approach required neither the use of sophisticated instrumentation nor the presence of metal ions other than the Pd (II) chloride complex. This gave maximum growth efficiency and eliminated contaminations of the deposit rendering the Pd deposition green. CV of H_{UPD} and Cu_{UPD} measured Pd film roughness. The CV results showed smooth Pd films up to 30 SLRR cycles followed by a rapid transition to dendritic growth at higher thickness. The quasi-2D growth, resulting in smooth and uniform Pd-film could also be confirmed up to 20 SLRR cycles by *in-situ* scanning tunneling microscopy. This kind of facile SLRR approach for contamination-free Pd deposition offered unsurpassed simplicity that could also be extended to other conductive substrates featuring strong H affinity [63].

One-cell type setup was used to improve the efficiency and deposition quality compared to multiple immersions or flow cells in developing a SLRR protocol for UPD of Pb layers for the growth of epitaxial and continuous Pt-thin films on poly and single crystalline Au surfaces. Quartz-crystal microbalance, and open circuit chronopotentiometry experiments demonstrated steady displacement kinetics and a yield that was higher than the stoichiometric Pt(II)−Pb exchange ratio (1:1). This kind of high yield was attributed to oxidative adsorption of OH_{ad} occurring on Pt along with the displacement process. *Ex-situ* STM measurements revealed that just after the first replacement event a dense Pt-cluster network was produced covering the Au-surface homogenously. Thereafter, Pt films grew homogenously with no significant changes in the cluster distribution and surface roughness observed up to 10 successive replacement events. XRD analysis showed distinct (111) crystallographic orientation of thicker Pt films deposited on (111) textured Au thin films. Coarse energy dispersive spectroscopy measurements and finer X-ray photoelectron spectroscopy measurements suggested at least 4 atom % Pb incorporated into the Pt layer compared to 13 atom % alloyed Cu when the growth was carried out by SLRR of Cu UPD [64].

The SLRR processing was successfully used in developing 2D-Pt/Pb nano alloys with controlled thickness, composition, and structure for determining their electrochemical behavior as a function of alloy composition. A single-cell, two-step SLRR protocol based on the galvanic replacement of upd-monolayers of Pb with Pt was used to grow epitaxial $Pt_{1-x}Pb_x$ ($x < 0.1$) alloys of up to 10 ML thickness on Au substrates. It was shown that by varying the terminating potential of the galvanic replacement step, the Pb atomic content could be controlled. Electrochemical analysis of the alloys showed that the adsorption of both H and CO exhibited similar, and systematic, decreases with small increases in the Pb content. These measurements, commonly used in electro-catalysis for the determination of active surface areas of Pt, suggested area-values much lower than those expected based on the net Pt-composition in the alloy as measured by XPS. These results showed that Pb has a strong screening effect on the adsorption of both H and CO. This also demonstrated the usefulness of the SLRR method, which could be employed in the design of 2-dimensional bimetallic Pt nano alloys for fundamental studies of electro-catalytic behavior in fuel cell reactions dependent on the nature of alloying metal and its composition [65].

Monocrystalline Au is an excellent substrate for electrochemical epitaxial deposition but the high cost of bulk crystals is not favorable to use in practical applications. Instead, ultrathin Au epitaxial films electrodeposited onto Si(111), Si(100), and Si(110) wafers serve as an inexpensive alternative for depositing epitaxial cuprous oxide (Cu2O) films. Such Au films from 8 to 28nm were deposited within

5 to 30 min. Films on the Si (111) were smoother with lower mosaic spread compared to those deposited onto Si (100) and Si (110). The mosaic spread of the Au (111) layer on Si (111) was only 0.15° for a 28.3nm thick film. The films onto degenerate Si (111) exhibited ohmic behavior, whereas those onto n-type 1.15 Ω•cm Si (111) wafers produced rectifying contacts with a barrier height of 0.85eV. The Au and Cu_2O films deposited on Si (100) and Si (110) were twinned with [221] and [411] orientations. This method could provide thin Au films as high-quality substrates for the deposition of a wide variety of epitaxial materials [66].

EC-ALD, although a low-cost semiconductor growth technique for fabricating display and photovoltaic devices, could also be employed in depositing metals and non-metals monolayers under surface limited deposition mode of under potential deposition of chalchogenide thin films. Initial studies of zinc and cadmium compounds were undertaken in this context for their suitable optical and electronic proprieties. In particular, cadmium chalchogenide thin-films are found suitable in manufacturing of last generation photovoltaic devices. Exploring new compounds seems significant due to the economic and low-environmental impact elements such as Cu, Sn, Fe and Zn. In particular, quaternary semiconducting materials based on the kesterite (Cu_2ZnSnS_4) structure are the most promising candidates to overtake the current generation of light-absorbing materials for thin-film solar cells [67].

Compound semiconductors were prepared using EC-ALD by alternating upd of the metallic/nonmetallic elements. The cycle is repeated several times to build up films with sub-micron thickness. High quality crystalline Cu2S ultra-thin films on Ag (111) was reported showing a well ordered layered crystal structure made on alternating pseudohexagonal layers. EC-ALD process results in the growth of highly ordered and almost unstrained ultra-thin films. This growth can lead to the design of semiconductors with optimal transport proprieties by an appropriate doping of the intra metallic layer. The present study enables EC-ALD as an efficient synthetic route for the growth of semiconducting heterostructures with tailored properties [68].

A novel electrolyte based on CuSO4 complexed by $K_4P_2O_7$ and $AgNO_3$ complexed by KI was studied for the deposition of CuAg alloys having a range of Ag compositions between 3%at. and 16%at under non stirred conditions at 50°C. The electrochemical characterization of the solution is also reported [69].

Growth of metal/oxide nanowires inside of semiconducting nanotubes has several applications, such as: electrodes for energy storage and energy conversion devices, and sensors. Electrodeposition of nanowires within the oxide nanotubes requires fine-tuning of the electrolytic solution as well as other deposition parameters because of the very high aspect ratio, and the semiconducting nature of the nanotubes. Electrodeposition of copper within nano trenches was reported for electronic interconnect applications. However, the aspect ratios of the trenches were lower than that of nanotubes and a seed metal barrier layer was present in the Damascene process that improved conductivity for copper deposition. Growth of metal NWs by electrodeposition onto a large nanoporous surface of anodic aluminum oxide (AAO) was also reported [70].

AAO is an insulator and one surface is metallized for growth of nanowires. Little work has been done in the area of electrodeposition of nanowires inside of semiconducting oxide nanotubes. Growth of Cu NWs inside of TiO_2 NTs ws reported. The TiO_2 NTs (length: 300-400 nm, and diameter: 70-110 nm) were prepared by anodization of a 0.2 mm thick Ti foil. The TiO_2 NTs were annealed in air at 450°C to have a high electrical resistance. In order to facilitate the bottom-up growth of Cu NWs, the base of the TiO_2 NTs were cathodically polarized to increase the conductivity locally. The base solution for Cu deposition was $CuSO_4$ and H_2SO_4. The accelerator and inhibitor additives used in experimens were (0.5 to 2 mM) NaCl, (0.5 to 2 mM) NaF, (25-100 μM) bis(3-sulfopropyl) disulfide (SPS), (44-176 μM) ethylene glycol (EG), (44-176 μM) polyethylene glycol PEG, (50-200 picomolar) polyethyleneimine (PEI). These were added individually and in mixed groups to determine the electrochemical characteristics of each additive. The other experimental variations/parameters investigated were: temperature of the solutions, and stirring conditions (mechanical vs. ultrasonication) [71].

Formation and properties of Cu film deposited on Ru/p-SiCOH/Si substrate were reported with high aspect ratio trench using EC-ALD. The conformability and step coverage of the deposited Cu film were elucidated to reach high gap fill capability as Cu interconnects for microelectronics. ECALD could be used to fabricate Cu metallized film by combining underpotential deposition, and surface-limited redox replacement (SLRR). Consequently, this work elucidated the effect of a fixed Pb-UPD potential and pulse Pb_{UPD} potential on the gap-filling capability and electrical properties of resulting Cu film on the substrate. Layer-by-layer deposition of Cu film formed at a Pb_{UPD} of - 443 mV exhibited higher conformability, and step coverage, and (111) texture. The results of this study suggested that the EC-ALD can used for fabricating Cu interconnects [72].

Harnessing cathodic hydrogen atom generation, metals such as Pt, Pd, Cu, Au and Ni were directly electrodeposited on functionalized dielectric layers of 6nm thick silicon oxide formed by thermal oxidation of *c*-Si substrate. Modifying the oxide layer with functional molecules and Au nanoparticles by simple wet chemistry, electrodeposition could be enhanced efficiently and thereby electroplate nanoparticles of Pd and Pt to obtain such thin metal films. In particular, Au nanoparticles on amine-modified silicon oxides remarkably enhanced electrodeposition of metal NPs to create sturdy metal films on the dielectric layer, n^+-Si/SiO_2-NH_2. Such enhancement is ascribed to good affinity of Au NPs with electrodeposited metal as well as enhanced current density across the silicon oxide. For an example, one-step electrodeposition of Pd film on dielectric layers was demonstrated in fabricating conductometric hydrogen gas sensor without transferring Pd film [73].

A comprehensive study of CdTe thin films was carried out using cadmium sulfate, cadmium nitrate and cadmium chloride precursors, in order to select the best electrolyte. Further, attempts were made to eliminate the reference electrode, since this could be a possible source of detrimental impurities, such as K^+ and Ag^+ for CdS/CdTe solar cells. A comparison of two and three electrode results were made from the results obtained from CdTe layers. Thin films were characterized using a wide range of analytical techniques for their structural, morphological, optical and electrical properties. These layers have also been used in device structures; glass/FTO/CdS/CdTe/Au and CdTe from both methods have produced solar cells to date with efficiencies in the region of 5%–13%. Comprehensive work carried out to date produced comparable and superior devices fabricated from materials grown using 2E system [74].

Possible Applications of ECALE

The low-cost deposition of a variety of EC-ALD materials is spreading very fast globally. The nano films already formed successfully include: most of the II-VI compounds including ZnSe, CdTe, and CdS, III-V compounds like InAs, IR detector materials InSb, and HgCdTe; thermoelectric materials such as the IV-VI compounds PbS, PbSe, and PbTe, as well as $SbTe_3$ and Bi_2Te_3, and the photovoltaic materials like CdTe, Ge, CIS, and CIGS. The elemental deposits of metals, reported recently, have been formed using a cycle called surface limited redox replacement (SLRR). Metal films deposited using an SLRR included - Pt, Ag, Cu, Pd, and Ru [29].

Current progress in fabricating EC-ALD based CdTe/CdS thin films for PV-energy conversion was explored in a recent doctoral thesis. The desired film thicknesses were achieved by exploiting the electrochemical surface limited reactions involved in forming a compound layer by using alternate and repeated UPD of one element onto the other. It was thus possible to optimize the EC-ALD process by using right combination of solution compositions, pH, and deposition potentials for each element in each cycle. The utility of such a process was examined by fabricating PV devices in substrate and superstrate configurations. However, the superstrate structure of ITO/CdS/CdTe composition was noted delaminating from the glass substrate due to interlayer stress. Whereas the substrate configuration of the same with Au on glass as the back contact had 200 nm (~600cycles) of EC-ALD grown CdTe, 80nm of CdS, and 100nm magnetron sputtered ITO to serve as the front contact. Such structures demonstrated J_{max} ~ 0.65 mA/cm^2 comparable to modern devices with $1/10^{th}$ of the material [75].

Ge nano films were deposited epitaxially using aqueous self-limiting mode of EC-ALD depending on the pH. The deposition cycle involved a Ge atomic layer deposited onto Te atomic layer formed on Ge via UPD. Te atomic layer was subsequently stripped from the deposit, leaving the Ge completing the cycle. Te atomic layer was thus employed as bait for Ge deposition, after which the Te was removed forming a soluble telluride. Deposit thickness was a linear function of the number of cycles. Raman spectra confirmed the formation of an amorphous Ge film, consistent with the absence of a XRD pattern. Films were more stable and homogeneous when formed on Cu substrates, than on Au, due to larger hydrogen over potential, and the corresponding lower tendency to form bubbles [76].

Somewhat closer to a large area manufacture of Ge thin films was demonstrated on silicon (Si) wafers without requiring high temperature, gaseous precursors, or complex apparatus in aqueous solution of electrochemical liquid phase epitaxy (ec-LPE) at low temperatures ($T \leq 90$ °C). A new cell design involving a compression of a liquid metal electrode into a thin cavity could enable the deposition process. Resultant features like epitaxial structure, low strain, and crystallographic defect content of the films were analyzed by electron backscatter diffraction, scanning transmission electron microscopy, high resolution X-ray diffraction, and electron channeling contrast imaging [77].

An electrochemical liquid–liquid–solid (ec-LLS) process was reported producing crystalline silicon at low temperature (80°C) without any physical or chemical template. Electro reduction of dissolved $SiCl_4$ in propylene carbonate using liquid gallium pool acted as the working electrode consistently yielding crystalline Si. X-ray and electron diffraction data separately indicated that the as-deposited materials were crystalline with the expected patterns for a diamond cubic crystal structure. SEM/TEM revealed the as-deposited materials (without annealing) to be faceted nano crystals with diameters in excess of 500 nm. Energy-dispersive X-ray spectra further showed no evidence of any other species within the electrodeposited crystalline Si. Raman spectra separately showed that the electrodeposited films on the Ga (*l*) electrodes were not composed of amorphous carbon from solvent decomposition. The cumulative data supported two primary contentions - first, a liquid-metal electrode served simultaneously as *both* a source of electrons for the heterogeneous reduction of dissolved Si precursor in the electrolyte (i.e. conventional electrode) *and* a separate phase (i.e. a solvent) that promoted Si crystal growth. Second, ec-LLS could be exploited for direct production of crystalline Si at much lower temperatures than ever reported [78].

Direct epitaxial growth of single-crystalline Ge nano wires at room temperature was performed on conductive wafers immersed in an aqueous bath in an electrochemical liquid–liquid–solid (ec-LLS) process involving the electro reduction of dissolved GeO_2 (aq) in water at isolated liquid gallium (Ga) nano droplet electrodes resting on single-crystalline Ge or Si supports. Ge nano wires were electrodeposited on the wafer scale (>10 cm^2) using only common glassware and a digital potentiostat. High-resolution electron micrographs and electron diffraction patterns from the cross sections of individual substrate-nanowire contacts in addition to scanning electron micrographs of the orientation of nanowires across entire films on substrates with different orientations supported the epitaxial nanowire growth. Energy dispersive spectroscopic elemental mapping of single nano wire indicated the Ga(l) nano droplet remaining affixed to the tip of the growing nano wire throughout the electrodeposition process. Current–voltage responses measured across many individual nano wires yielded reproducible resistance values. The presented data cumulatively showed epitaxial growth of covalent group IV nanowires from the reduction of a dissolved oxide under purely bench top conditions [79].

A new electrochemical strategy was described for direct growth of crystalline group IV and III–V semiconductors at or near ambient temperature. This employed the semiconductor solvation properties of liquid metal melt with the utility and simplicity of conventional electrodeposition. A low-temperature liquid metal (i.e. Hg, Ga, or alloy) acted as the source of electrons for the reduction of oxidized semiconductor precursors dissolved in an electrolyte as well as the solvent for dissolution of the zero-valent semiconductor. The super saturated concentration of the semiconductor in the liquid metal triggered the crystal nucleation and growth. In this way, the liquid electrolyte–liquid metal–solid crystal phase boundary influenced the crystal growth with many useful features for preparing covalent semiconductor crystals. First, it did not require high temperatures, toxic precursors, or high-energy-density semiconductor reagents, which simplified the equipment complexity and cost. In practice, it required only a beaker filled with electrolyte and an electrical circuit. The process is compatible with thermally and chemically sensitive substrates (e.g., plastics) that could not be used as substrates in conventional syntheses of covalent semiconductors. Second, it could be controlled over a host of crystal shapes and sizes by changing the common parameters. Large and small semiconductor crystals were grown both homogeneously within a liquid metal electrode

and heterogeneously at the interface of a liquid metal electrode and a seed substrate. Third, the rate of introduction of zero-valent materials into the liquid metal was precisely controlled by the applied potential/current. Thus, the proposed ec-LLS process was found as a established platform for preparing Ge and Si crystals from bulk ($1cm^3$), micro ($10–10cm^3$), and nano-sized ($10–16cm^3$) liquid metal electrodes in common solvents at low temperature [80].

Crystalline GaAs was prepared directly by electro reduction of As_2O_3 dissolved in alkaline aqueous solution at a liquid gallium (Ga(l)) electrode at modest temperatures ($T \geq 80°C$). Ga(l) pool electrodes yielded consistent electrochemical behavior resulting in repetitive interdependences of applied potential, concentration of dissolved As_2O_3, and electrodeposition temperature on the quality of the resultant c-GaAs (s). Raman spectra based composition of the resultant film was found strongly dependent on both the electrodeposition temperature and dissolved concentration of As_2O_3 but not on the applied bias. For electro depositions performed either at room temperature or with high (≥0.01 M) concentrations of dissolved As_2O_3, Raman spectra of the electrodeposited films were consistent with amorphous As(s). X-ray diffractograms of As(s) films collected after thermal annealing indicated metallurgical alloying occurring at temperatures in excess of 200°C. Optical images and Raman spectra showed the composition of the as-electrodeposited film in dilute (≤0.001 M) solutions of dissolved As_2O_3 (aq) was pure c-GaAs(s) at much lower temperatures than 200°C. Diffractograms and transmission electron microscopy performed on as-prepared films confirmed the c-GaAs(s). The collective results thus provided the first clear proof of an ec-LLS process involving a liquid metal that served simultaneously as an electrode, a solvent/medium for crystal growth, and a co-reactant for the synthesis of a polycrystalline semiconductor [81].

Electrodeposition of solar cell absorber layers of $Cu_2(Sn,Ge)S_3$ with metallic precursors and subsequent annealing was found useful for single junction thin film solar cells, already demonstrating PCE of 6.7%. In absence of adequate knowledge of the aqueous electrodeposition of metallic Ge, a method was evolved for the growth of germanium-containing precursors for $Cu_2(Sn,Ge)S_3$ using propylene-glycol electrolytes without additives, giving rates of germanium electrodeposition higher than other plating baths and are economical. The electrochemical behaviour of copper, tin and germanium in propylene glycol was studied with detail measurements of smooth and compact layers of each of the pure elements. The co-electrodeposition of Cu and Ge was studied to deposit alloy Cu_3Ge films with constant [Cu]/[Ge] ratio of around 3 over a wide potential range, with a higher plating efficiency than that of pure germanium. For these reasons, Cu and Ge were incorporated into the precursor via the referred co-deposition method. After thermal annealing in the presence of elemental S, the semiconductor $Cu_2(Sn,Ge)S_3$ was successfully formed and it was incorporated in a working solar cell structure with efficiency of 0.7% [82].

The electrochemical co-deposition of Cu-Ge thin films from an alkaline tartrate electrolyte was reported by combining cyclic voltammetry and quartz crystal microbalance of the unitary and alloy electrolytes. Ge undergoes reduction from Ge4+ ($GeO_3^{\ 2-}$) to Ge^{1-} (GeH) in a two-step process forming a self-limiting deposit thickness as a function of the Ge ion concentration and pH. Cu^{2+} deposition was strongly inhibited by the presence of Ge species above −1.2 V Ag/AgCl, while at more negative potentials a signature of alloy co-deposition was found, in parallel with hydrogen evolution. Oxygen deposition is significant when Ge is at or above 25at%. Induced codeposition was rationalized in terms of the activation of the Ge-H bond by Cu, resulting in the formation of adsorbed species containing H-Cu-Ge, whereby H is dissociated, resulting in alloy growth in parallel with formation of a significant amount of H_2 gas [83].

Growth of Ge filamentous structures was reported from an aqueous electrolyte at various temperatures using In and Sn NP arrays as nucleation sites. The temperature of Ge cathodic deposition process from aqueous solutions could significantly affect the layer structure deposited onto the surface. In the presence of metal particles in the molten state, filamentous Ge structures grew due to the cathodic reduction of Ge-containing ions on the electrode surface, followed by dissolution and crystallization in the melt at the substrate interface [84].

The electrochemistry of the germanium (II) tri-halide anions, $[GeCl_3]^-$, $[GeBr_3]^-$ and $[GeI_3]^-$ was reported in supercritical difluoromethane containing 60 mm $[N\textit{n}Bu_4][BF_4]$ at 19.1MPa and 358K. The voltammetry showed mass-transport-limited currents for reduction to germanium at gold on the first scan. There was no evidence of a Ge stripping peak and, on subsequent scans, the electrode slowly got passivated with the deposition of approximately 0.4μm of material. The redox potentials for the reduction of the three tri-halides were in the order as - $[GeCl_3]^- < [GeBr_3]^- < [GeI_3]^-$, with the iodide being the most easily reduced complex. Electrodeposition of Ge onto TiN electrodes from supercritical difluoromethane at 19.1MPa and 358K, using either 16mm [EMIM] $[GeI_3]$ with 60mm $[EMIM][BF_4]$ or 16mm $[N\textit{n}Bu_4][GeI_3]$ with 60mm $[N\textit{n}Bu_4][BF_4]$, gave deposition rates of 2–3μm/h. Raman and TEM measurements the Ge films to contain nano crystals of Ge embedded in an amorphous Ge matrix [85].

The usefulness of ballistic hot electron injection into solutions for depositing thin group-IV films was reported in a dripping scheme in which a very small amount of $SiCl_4$ or $GeCl_4$ solution was dripped onto the surface of a nanocrystalline Si (nc-Si) electron emitter. The emitter was driven without using any counter electrodes. It is shown that thin Si and Ge films were deposited onto the emitting surface. Spectroscopic surface and compositional analyses showed no extrinsic carbon contaminations in deposited thin films, in contrast to the results of a previous study using the dipping scheme. The availability of this technique for depositing thin SiGe films was subsequently demonstrated using a mixture $SiCl_4$+$GeCl_4$ solution. Ballistic hot electrons injected into solutions with appropriate kinetic energies promoted preferential reduction of target ions with no by-products leading to nuclei formation for the thin film growth. Specific advantageous features of this clean, room-temperature, and power-effective process was described in contrast to the conventional dry and wet processes [86].

The fabrication and characterization of CdS/TiO_2 nanotube-array coaxial heterogeneous structures was reported for their applications in various photo catalytic fields, such as water photo catalytic decomposition and toxic pollutant photo catalytic degradation. Thin films of CdS were conformally deposited onto TiO_2 nanotubes using a modified method of EC-ALD to promote the deposition of CdS onto the TiO_2 tube walls while minimizing deposition at the tube entrances, thus preventing pore clogging. The coaxial heterogeneous structure so prepared significantly enhanced CdS/

TiO_2 and CdS/electrolyte contact areas and reduced the distance that holes and electrons must travel to reach the electrolyte or underlying conducting substrate. This could enhance photon absorption and photocurrent generation. In comparison to a pure TiO2 nanotube array, a 5-fold enhancement in photo activity was observed using the coaxial heterogeneous structure [87].

Using different upd chemistries EC-ALD of CdTe was carried out onto different substrates like Au, Ni, Cu, Ag, Ge, and Mo. Deposits of 100 cycles were examined with characterization techniques like electron probe microanalysis (EPMA) X-ray diffraction (XRD) and spectroscopic ellipsometry (SE). The observed results confirmed that when the substrate used could oxidatively dissolve into ions, the resulting deposits were of inferior quality, otherwise high quality deposits were obtained on passivated substrates. The poor quality depositin was assigned to the codepositing ions forming chalcogenide impurity. In a combined setup of the automated flow cells and three electrode cell with a Ag/AgCl reference electrode was controlled by a potentiostat. In between two succesive cycles oxygen was purged out by nitrogen bubbling, to minimize O_2 in the system. The electrodes used in these studies were polycrystalline Au on glass, with a 50 nm Ti adhesion layer. Cd was electrodeposited from a solution containing 0.5 mM $CdSO_4$ in 0.5 M $NaClO_4$, @ pH3. Te was electrodeposited from one of the two solutions (i.e. either 0.1mM TeO_2 in 0.5 M $NaClO_4$, pH3, or 0.1 mM TeO_2 in 0.5M $NaClO_4$ buffered with 50 mM sodium borate pH 9). The blank used for rinse was 0.5 M $NaClO_4$, pH3 to rinse out the cell of any precursors from previous solutions.

It was noted employing three different cycles (i.e. an acidic Te solution; an acidic Te-solution with a reductive Te-stripping step; and a basic Te solution with no stripping step) that acidic Te-chemistry involved 2 steps. The first step was Cd^{2+} ions being pumped into the cell at 18*m*L/*min* for 5 seconds at a potential of -550mV (Ag/AgCl). The solution was held for 15s of deposition, at the same potential, and allowing the system to come to equilibrium. The Cd^{2+} ions were then rinsed from the cell with the blank solution for 15s, concluding Cd deposition. For the Te step, a solution of $HTeO^{2+}$ ions were pumped into the cell for 5s at a potential of -200mV (Ag/AgCl) followed by an quiescent deposition for 15s, at the same potential. The $HTeO^{2+}$ ions were rinsed from the cell, using the blank solution, for 15 s, completing one cycle of CdTe. For introducing stripping step at the end of the cycle, the Te-deposition was shifted to 100 mV more negative. This included first rinsing with blank and then stepping the potential to -900mV for 15s, where Te atoms in excess of an atomic layer were reduced to a soluble telluride species that diffused away. This was followed by rinsing again with blank for 15s at the same potential to remove the telluride products. When using the basic Te-chemistry, the only difference was that the Te deposition potentials were changed to -800 mV.

This study could be used for studying the influence of ionic activity of the substrate versus oxide covered nonreactive substrate. Au has a passivating surface oxide layer without dissolving into ions. It is chemically stable and cleaned of any surface contamination. Crystalline stoichiometric CdTe was deposited exhibiting proper optical constants and similar growth rates. In contrast, Ni being a reactive metal oxidatively dissolved when the potential was positive of -400 mV (Ag/AgCl). In case of acidic deposition, the Te deposition potential was -200mV, this would strip the underlying Ni substrate to produce Ni^{2+} ions. These Ni^{2+} ions could subsequently redeposit as NiTe. This process could only occur until the CdTe deposit cover the Ni substrate preventing the oxidative dissolution of the Ni electrode. This exhibited excess of Te while remaining crystalline with close to proper optical constant.

The discrepancy between Ni and Au were attributed to the stripped Ni ions codepositing with Te ions forming NiTe increasing the relative amount of Te to Cd in the first cycles until the CdTe deposit passivates the underlying Ni. To circumvent the NiTe codeposition issue, a more negative Te deposition could be used for Te stripping chemistry. Te stripping emplyed a larger overpotential to deposit Te then the excess Te could be reductively stripped electrochemically by means of a two electron process. The Te^{2-} ions produced were water soluble and diffused away leaving behind a Te layer that was stabilized by compound formation.

In another scheme Te was deposited at a more negative potential without the use of a stripping step in case of basic Te solution. Te reduces from $HTeO^{2+}$ according to Nernst equation. By raising the pH the deposition potential of Te shifted more negative ensuring lesser Ni^{2+} ions. Results showed that best CdTe deposits on Ni were made with a basic Te solution.

Copper does not oxidatively strip until ~0mV (Ag/AgCl) and it should not have any issues while growing CdTe. Cu forms stable compounds with all of the chalcogenide species, so Te would be no exception.

Acidic conditions were used to deposit CdTe on a Cu substrate. When using an acidic Te solution, the deposits had very little Cd in them. The resulting deposit were more like Cu_2Te than CdTe. In this case it would seem possible that the formation of Cu_2Te is more favored than CdTe. If this wa the case then Cu_2Te would short circuit CdTe formation. The presence of Cu^{2+} ions short circuited the ECALD process. Thus, acidic chemistry was not found to work for Cu substrate as Cu^{2+} ions interfered. Using the basic chemistry improved the quality of the deposits. The stoichiometry improved drastically from 0.15 to 0.83, however, there still ws a significant Te excess in the deposit.

Silver is a fairly stable nonreactive metal. Like Cu, silver readily forms compounds with the chalcogenides, however, due to silver's more stable nature fewer ions should be present at negative potentials, which should prevent undesired compound formation. The first experiments on silver electrodes used the basic chemistry resulting in rough deposits with black color opposed to the smooth one having a purple color. EPMA elemental mapping showed that the bumps present there were most likely CdTe. In acidic chemistry the potentials used in the acidic deposition were negative enough so that the substrate should not have an effect on the deposition. However, the acidic chemistry also resulted in rough deposits with practically no Cd. CdTe EC-ALD onto Ag was found most difficult due to the influence of the Ag substrate. Adding Cl- could prevent Ag^+ dissolution improving the deposit quality.

Ge has been considered for a multijunction photovoltaic configurations. From this angle, the EC-ALD of CdTe onto Ge is important. Ge having oxidized surface needs some pretreatment before it is electrodeposited. For this, it was first dipped in HF to remove the oxide layer followed by ozone cleaning to remove organic contaminants besides growing thin surface oxide. Before

the EC-ALD, the surface oxide was therefore reduced at a negative potential. Ge is very reactive so positive potentials could not be used, thus basic Te was used to grow CdTe. High quality deposits were prepared similar to the quality achieved on a Au substrate. Like Au, Ge does not produce any ions to interfere with the deposition process as confirmed by EPMA analysis.

Mo is another important substrate as it is back contact metal for PV devices. Mo having a thick oxide layer, however, must be cleaned before it is electrodeposited. For this, Mo electrode was reduced at -1.2V (Ag/AgCl) for five minutes then basic Te chemistry was used because the acidic chemistry would have reoxidized it. The resulting process could not give a continuous film instead the depositions occurred in the form of small islands. These islands, though small, were CdTe having characteristic blue color.

The study of substrate chemistry influence on the deposition process produced special effects as noted in case of substrates like Au, Ni, Cu, Ag, Ge, and Mo. 100-cycle deposits of CdTe were grown onto each substrate and analyzed with EPMA, XRD and SE. Results indicate that substrates that could oxidatively dissolve and produce ions (Ni Cu Ag) hindered the EC-ALD process resulting in inferior quality films. Consequently, it was presumed that competing compound formation reactions could occur when ions produced by the oxidative dissolutions of the substrate were present within the solution. These reactions could potentially short circuit the EC-ALD process in the early cycles. Substrates that did not produce ions (Au, Ge, Mo) did not affect the process and grew the films of good quality, however, a surface pretreatment was found necessary in some cases for quality depositions.

2D-allotrope of Ge, germanene, was explored depositing using EC-ALD followed by characterization by STM and micro-Raman shift at 290 cm^{-1}. STM showed the formation of atomically flat terraces at negative potentials. The micro-Raman spectra clearly suggested the presence of an electrochemically grown germanene monolayer. This kind of germanene deposition holds promise as a low cost, flexible, room temperature technique for the production of compound semiconductors. This layer by layer growth affords superior control over thickness, homogeneity, crystallinity, and the overall quality of the deposit [88].

An automated flow cell with three electrodes was potentiostat controlled during deposition studies. The potentiostat, valves and pump were PC controlled. Polycrystalline Au on glass was used as electrode with a 50 nm Ti adhesion layer. The solutions used were 0.1mM $CuClO_4$ with 0.1mM SeO_2 in 0.5M $NaClO_4$, pH3 and 1.5 mM $Cu(ClO_4)_2$ with 1.5 mM SeO_2 in 0.5M $NaClO_4$, pH3. Electrochemical codeposition is considerably faster compared to the typical EC-ALD cycle. However, the diffusion of ions becomes very important for prolonged depositions, which might change the composition of the deposit over time. For taking care of these problems, a novel type of pulsed deposition was evolved for depositing chalcogenide based the rmoelectrics [89].

In case of CuSe, the irreversibility of Se and reversibility of Cu were exploited by pulsing sequence, where a fraction of a monolayer of Se is deposited and coated with bulk Cu in a cathodic pulse followed by removal of the bulk Cu with an anodic pulse leaving CuSe behind. A number of combinations of different parameters were attempted to get the optimum condition. A typical pulsing study employed a cathodic pulse to -100mV for 0.5 seconds could produce the desired coverage and an anodic pulse to 100mV for 2 seconds should strip any bulk copper formed. This process was repeated five times then the pump was turned on for 5 seconds to refresh the diffuse layer. This pulsing scheme was repeated for 1100 cycles when the deposit began to show color. EPMA shows that Cu_2Se was formed with an average Cu/Se ratio of 2.2 indicating slight excess of Cu.

After examining all of the combinations of the pulsing experiments it was found that the best deposits were grown using -50mV as the cathodic pulse and +50 as the anodic pulse. This was determined by the optical microscope. This chemistry gave a homogeneous deposit with no apparent Se overgrowth.

Monocrystalline layers are grown in all cases of pulse deposition. The bandgap of the Cu_2Se films was also estimated from SE by converting reflectance into absorbance spectrum. The direct bandgap of Cu_2Se is 1.7 which is consistent with literature values. Conclusion The proof of concept work in the formation of Cu_2Se by electrochemical pulse deposition is presented. Results show that Cu2.1Se is the predominate species formed despite the sequence used. The slight Cu excess is most likely due to the excess of Cu^{2+} ions created at the surface of the electrode during the anodic pulse, which do not have time to completely diffuse away. XRD results confirmed crystalline Cu_2Se. Excess selenium observed with the optical microscope was confirmed with XRD as well. SE results show an index of refraction of 1.9 as well as an average growth rate of 0.2mL per pulse with a direct bandgap of 1.7eV [89].

A novel method of growing thin films organic polyamid material was demonstrated using a cyclic repetition of two consecutive, complementary, self-limiting surface reactions. The molecular compounds that react with the surface were dissolved in an organic solvent. This new method demonstrated that ALD and MLD strategies of thin film deposition could benefit from changing from the gas phase to the liquid phase as a number of advantages were available from precursors. MLD was established using dissolved precursors in solution ALD (sALD) as a novel thin film coating technique. This has broadened the range of reaction chemistries accessible for ALD by employing activation, protection and deprotection of organic functional groups, which were not feasible in gas-phase thin film deposition (gALD/gMLD) because they rely on large and/or polar (ionic) species which cannot be converted into volatile form. The process of sALD, however, could take care of these limitations by exploiting a wide range of methodologies established elsewhere. For instance, an aromatic polyamide thin film was demonstrated with potential applications in the coating of fibers or other materials with outstanding mechanical and fire-retardant properties. However, it is expected that sALD/sMLD will be used as alternatives to the established thin film coating techniques in the semiconductor, energy conversion, and textile fields, to name a few. One could further envision that the mild conditions of sALD/sMLD processing, combined with the versatility and specificity of available dissolved reagents, would provide area-selective deposition and etching. For example, a protection/deprotection scheme might be used in area-selective deposition, whereas alkylation could be exploited to render a surface inert in area-selective etching [90].

Discussion and Conclusion

Despite optimizing the EC-ALD of CdS and CdTe on Au electrode for realizing more efficient PVSC devices, it is, however, not a cost

effective material for large-scale production due to involvement of gold. The extension of EC-ALD chemistry should therefore be attempted in case of other possible alternative metals. For instance, Mo being a good back contact material in fabricating CdS/CdTe PVSCs could be considered as a better choice as it is less expensive, and does not inter-diffuse into the subsequent structures degrading the quality. Mo has a very thick surface oxide that needs to be eliminated before deposition onto it. Investigating such treatments is an essential step for developing this chemistry. Realizing the important role of ECALD in cost effective fabrication of multi junction PV cells, it is desirable to fabricate each junction having unique interface, which would need special chemistry to grow the proper materials. The optimization of EC-ALD chemistries onto different materials is therefore necessary to explore further from this angle as well as an important area of future work.

There are numerous possibilities of developing different combinations of CdS deposition along with CdTe ECALD. It is equally important to study the influence of thermal annealing, CdCl2 treatments, fabricating substrate/superstrate configurations, and like that. The superstrate configuration must be further examined minutely to take care of delamination by improving the quality of ITO. Superstrate configuration PVSCs should be investigated further using better deposition quality of ITO and FTO - two major transparent conducting oxides used in CdS/CdTe based devices. Controlling fabrication processes would certainly affect both the methods of fabrication. Extremely thin layers involved in these studies have been quite prone to shunts. Possibly this could be avoided by using clean room fabrications [86].

Incidentally, the active region sufficient for adequate solar radiation absorption in 2nd generation PVSCs is around 2-3µm. For depositing such thick films by EC-ALD, it might take considerably longer duration of time (~ 48hrs). EC-ALD is in deed a too slow process for fabricating 2nd generation PVSCs. However, in 3rd generation PVSCs it requires average absorber layer thickness ~200 nm. In such applications EC-ALD processes are more applicable. In 3rd generation PVSCs the nanostructures are generally used to increase efficiency while reducing the amount of material used. For such cases, a deposition method that can produce high quality conformal deposits must be used. EC-ALD is ideally suited for this purpose [91].

One of the fturistic developments of thermoelectric materials has been attempting to reduce thermal conductivity decoupled from the electrical properties. The phonon scattering being at the root of different strategies include (i) disorder or distortion of unit cells, (ii) resonant scattering by localized rattling atoms and (iii) interface scattering. The construction of a 'natural superlattice' in thermoelectric materials was proposed by intercalating an MX layer into the van der Waals gap of a layered TX2 structure, which has a general formula of $(MX)_{1+x}(TX_2)_n$ (M = Pb, Bi, Sn, Sb or a rare earth element; T = Ti, V, Cr, Nb or Ta; X = S or Se and n = 1,2,3). One of the intercalation compounds $(SnS)_{1.2}(TiS_2)_2$ showed superior thermoelectric properties compared to pure TiS_2 in the direction parallel to the layers [92].

In addition, superionic semiconductors with two independent structural units allow separate modifications in tuning the electrical and thermal properties. For instance, by alloying Ag and Te in Cu_8GeSe_6, the *ZT* values were significantly improved to above unity at 800K in $Cu_{7.6}Ag_{0.4}GeSe_{5.1}Te_{0.9}$, comparable with the best superionic liquid-like thermoelectric materials. The ultralow thermal conductivity was attributed to the weak chemical bonding between Cu atoms and the rigid $[GeSe_6]$ sublattice [93].

These two examples of decoupled reduction of thermal conductivity show enough promise of the progress that is expected in these directions where EC-ALD technology is bound to give better results in times to come.

The utility of upd chemisry in realizing mono/multiple layer 2D-materials based structures has been found to be of great promise provided the strategy of decoupling thermal conductivity from electrical conductivity is realized in the developed multilayer structures including superlattices.

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