CHAPTER III

THEORY OF ELECTRODEPOSITION

3.1 INTRODUCTION

The art of electroplating metals and metallic alloys has been in practice for nearly a century and the earlier efforts are well documented. Most of the development has been more by way of art rather than science, which started to merge only recently. Further the viability of using the electrodeposition technique as a tool of material technology is attracting attention as a means of obtaining films of a wide variety of materials including semiconductors, superconductors, polymer films, materials for biostimulation, specific electronic device application materials and others.

Some of the key advantages of the electrodeposition technique are

1. It is possible to grow films over large areas as well as irregularly shaped surfaces.
2. Compositionally modulated structures or non-equilibrium alloys can be electroplated.
3. A wide range of industrial experience can be drawn upon.
4. It is especially attracted in terms of cost, high throughput and scalability.

Electrodeposition was originally used for the preparation of metallic mirrors and corrosion resistant surfaces among other things. In its simplest form electrodeposition consists of an electrolyte containing metal ions, an electrode or substrate on which the deposition is desired, and a
counter electrode. When a current flows through the electrolyte, the cations and anions move towards the cathode and anode, respectively, and may deposit on the electrode after undergoing a charge transfer reaction. The discovery of electrodeposition can be traced back to Michael Faraday and his famous laws of electrolysis.

The first law states that the total amount of chemical change produced by an electric current is proportional to the total charge passing through the electrolyte. The second law states that the masses of the different substances liberated in the electrolysis are proportional to their chemical equivalent weights.

3.2 ELECTRODEPOSITION SYSTEM

A simple electrodeposition system consists of the following components:

3.2.1 Electrolyte

The electrolyte or bath provides the ions to be electrodeposited. It has to be electrically conductive, it can be aqueous, non-aqueous or molten; and it must contain suitable metal salts. Sometimes an additive is included to improve the quality of the electrodeposits. An ideal additive should not become incorporated in the film but should lead to improvement of its adhesion, surface finish, uniformity etc.

3.2.2 Electrodes

At least two electrodes (cathode and anode) are needed. An applied electric field across these electrodes provides the main driving force for the ions. The positive and negative ions deposit at the cathode and anode
respectively. Cathodic deposition is more popular in electroplating because (1) most metal ions are positive ions and (2) anodic deposition has been found to give poor stoichiometry and adhesion.

3.2.3 Power Supply

The power supply can be (1) direct current at constant voltage, which leads to potentiostatic deposition, (2) direct constant current which leads to galvanostatic deposition or (3) a current or voltage waveform or pulse.

The process leading to electrodeposition can be outlined in simple terms as below. On the application of an electric field, $M^{n+}$ would move to the cathode, and the chemical electrodeposition process can be written as

$$M^{n+} + ne \rightarrow M$$

On the other hand, if the electrolyte contains more than one species that can be simultaneously deposited, then the electrodeposition process, for, say, two types of ionic species can be written as

$$M^+ + e \rightarrow M$$
$$N^+ + e \rightarrow N$$

Or

$$M^+ + N^+ + 2e \rightarrow MN$$

Accordingly a compound or alloy of a multicomponent system can be deposited we can deposit a compound or an alloy of a multi-component system.
As the electrodeposition proceeds, the ionic concentration in the bath is depleted and has to be replenished by adding the salt. Another alternative is to use one of the electrodes as a sacrificial electrode, one that corrodes during electrodeposition to maintain the ionic concentration constant.

The ionic discharge process can be summarized as follows

1. Ionic species move in the electrolyte bulk toward the electrode on which the deposition is to occur. This is regarded as the reactant zone.

2. The moving ionic species approach the electrode (prereaction site) at, say, the outer Helmholtz plane (OHP) without actually being discharged. The charge transfer that ultimately leads to electrodeposition starts at this interface. This is regarded as the charge transfer zone.

3. The charge transfer is completed at the electrode, and the electrodeposit is obtained.

According to the Butler-Volmer model, the discharge of the electroplating ions is assumed to take place only when the latter have arrived at the outer Helmholtz plane. While calculating the rate of charge transfer reaction, it assumes that the rate at which the ions are consumed by the discharge reaction is equal to the rate at which they arrive at the OHP. In the charge transfer zone or pre-reaction zone the ions are transported from the electrolyte bulk to be discharged at the electrode. The concentration term in the Butler Volmer equation should be the ionic concentration in the charge transfer zone at $x = 0$, i.e., $c_{x=0}$ and not the bulk concentration $c^0$ at $x = \infty$. The two will be equal only when the ionic discharge rate is equal to the rate of
ionic transport. If the charge transfer rate is greater than the rate of ionic transport, then the interface region will become depleted of the discharging ionic species. On the other hand, if the ionic transport processes are much faster, this will lead to the accumulation of ions in the interface region. This inequality between the transport flux and the charge transfer flux gives rise to concentration polarization or overpotential.

3.3 IMPORTANCE OF DIFFUSION LIMITED TRANSPORT

Diffusion limited transport has been found to be useful in electrodeposition work. A discussion of the important implications follows.

Diffusion limited transport enables oppositely charged ionic species to move in the same direction. One can thus perform cathodic electrodeposition with negatively charged ions also. Diffusion limited transport enables one to change the equilibrium potential over a range of values depending upon the ionic activities. According to Nernst equation, a decrease in ionic activity of the discharging species results in a negative shift in the deposition potential. This possibility has been used by a number of workers to electrodeposit two or more components with different equilibrium potentials.

The current density under the influence of diffusion is given by

\[ j = j_1 \left[ 1 - \exp \left( \frac{\alpha F \eta}{RT} \right) \right] \]  \hspace{1cm} (2.1)

Suppose in a cathodic electrodeposition experiment the electrode potential is continuously driven in the negative direction. Initially when the electrode potential is made more negative than the equilibrium potential of the ionic species transported by diffusion, the current will rise. The cathodic
current will continue to rise with increasingly negative electrode potential, and the interfacial ionic activity will decrease continuously. When the rate of diffusion becomes equal to the rate of discharge, the interfacial ionic activity will be practically zero and the current density will attain a value \( j_l \). The higher efficiency of the cathodic process results from the higher value of \( j_l \). This value can be increased by (1) increasing the concentration (2) increasing the diffusion coefficient by working at a higher temperature, and (3) lowering the diffusion layer thickness by forced convection (stirring).

3.3.1 Transfer Coefficient

In the derivation of the Butler – Volmer equation, the movement of ions across the interface was assumed to be the only necessary condition for the charge transfer reaction. The role of electrons in the metal electrode as dynamic entities capable of crossing the interfacial barrier was completely ignored. The electron in general quantum mechanically tunnel through the interfacial barrier to the ionic species in the electrolyte [47-49]. As the electron transfer process is non-radiative, the tunneling should take place without a change in the energy of the system within the restraints of the uncertainty principle. This requires sufficient stretching of the bonds between the reactant and the surrounding ligand to create an acceptor state of energy equal to the electron energy in the metal.

The transport coefficient (symmetry factor) \( \alpha \) for quantum mechanical tunneling has been defined as the ratio of the energy required to stretch the ion ligand bond to the critical state and the energy gap between the electron state in the metal and the solution side of the interface. The energy gap should be closed to make tunneling possible. It can be seen that \( \alpha \) is correlated to some physically meaningful parameters such as the ion-solvent interaction and the structure of the double layer.
The charge transfer reaction activated by a bridging ion can be treated quantum mechanically. In bridge assisted tunneling, the transmission probability may be large. Also if the bridging ion is of opposite charge to reacting species, this may lead to a higher concentration of the latter at the OHP.

### 3.3.2 Surface Coverage Factor

The electrode surface immersed in the electrolyte is generally with contact adsorbed ions, solute molecules etc., is broadly of two categories: non blocking and blocking. The effect of blocking species can be incorporated into the Butler-Volmer equation by considering only the fraction $\theta$ of the electrode surface that is not available for charge transfer reaction when a current $j$ is flowing. $\theta$ is called the surface coverage factor for all adsorbed species. Frumkin [50] gave a detailed account of the role of contact adsorption in the electrode process.

The binding energy of the contact adsorbed species is of practical interest in electrodeposition. For example, during aqueous electrodeposition, the discharging hydrogen is often strongly bound to the cathode surface with energy on the order of 50 kcal/mol. On the other hand the water molecules are only weakly adsorbed. Interfacial tension has also been used as a parameter to express the interaction of the solvent-electrode system.

Many non-aqueous solvents interact fairly strong with the electrode surface and $\theta$ become a dominant factor. Apart from solvent adsorption, the role played by the contact-adsorbed additives is also significant in controlling $\theta$ (and hence the electro-deposition).
Multi step reaction

For a single step reaction,

\[ r + 2e \rightarrow p \]

The above reaction may comprise two steps

\[ r + e \rightarrow I \]
\[ I + e \rightarrow p \]

where I refers to an intermediate species formed during the reaction.

Generally the step with the lowest exchange current density qualifies as the rate determining step (RDS). Suppose \( j \) is the current density corresponding to the RDS for a \( s \) – step reaction. The total current density would be \( sj \). The electrode potential will have only one value, but the overpotentials corresponding to the \( s \) different steps may be different. The over potential is the difference between the electrode potential and the reverse potential. The different values for overpotential can be attained at different steps simply because of the differences in the reversible potentials of each step, which are governed by the respective concentration ratios of the intermediates.

The exchange current density \( j_o \) and the transfer coefficients \( \alpha_c \) and \( \alpha_a \) are two important parameters related to the kinetics of the charge transfer reaction. For a given electrode potential, the net current density will be higher for the process with the higher exchange current density. The exchange current density depends on the nature of the reaction, the electrode material, and the bath composition. The transfer coefficient describes the effect of the
electric field on the charge transfer step and the symmetry of the cathodic and anodic processes. Its dependence on the electrode material is usually small.

3.4 ELECTRODEPOSITION OF SEMICONDUCTORS

In principle the theory of metallic electrodeposition can be applied to semiconductor film deposition. However, some problems of typical of semiconductors have to be considered.

First, semiconductor films are relatively resistive (in comparison with metals). As a consequence, the interfacial potential and charge distribution may drastically change over the first few layers of semiconductor. For thicker films this may even lead to morphological changes.

Second, the resistivity of a semiconductor is highly sensitive to defects, orientation, and other factors. As the electrodeposition proceeds, the semiconductor resistivity may continue to vary. In an extreme situation, a non degenerate semiconductor may even become a degenerate semiconductor.

Third, in metal electrode – electrolyte contact, the space charge layer within the electrode plays an insignificant role, whereas for semiconductor electrolyte contact the space charge layer is dominant.

Fourth, the presence of the space charge layer, the high density of surface states or surface defects, and the resistivity of the semiconducting film can also exercise controlling effects on the charge transfer reactions. As a result the Tafel plot for semiconductors may not be the same as was originally envisaged for metallic deposits.

The above remarks are applicable to both elemental and compound semiconductors. Apart from a few elemental semiconductors (Si, Ge, Se, Te)
most of the semiconductors of interest are compound semiconductors. The three problems of a typical compound semiconductor electrodeposition are

1. Most of the compound semiconductors have at least one metallic (Ga, Cu, In, Cd, Zn, etc..) and one nonmetallic (S, Se, Te, P, As etc..) component as in GaAs, GaP, CdS and CuInSe$_2$. Unfortunately, the reduction potentials of the nonmetals are widely different from those of the metal ions. The general condition for co-depositing the different components of the compound requires that the constituents have equal reduction potentials. This is difficult to attain for compound semiconductors.

2. Most compound semiconductors have a very negative Gibbs free energy of formation. This may shift the deposition potential of the more noble component to more positive value, helping the co-deposition.

3. Many compound semiconductors exhibit multiple phases. The possibility of such multiphase formation may lead to additional complexities in the activity term controlling the electrodeposition.

3.5 PRACTICAL ASPECTS OF ELECTRODEPOSITION

3.5.1 Choice of substrate

Substrates in semiconductor electrodeposition are expected to play an important role. Their characteristics are not restricted to impart certain morphological characteristics to the growing layer. In a more subtle way electronic or optical properties may also be affected. Therefore, in choosing a
suitable substrate, in addition to considering the need to provide mechanical support to the electrodeposits, due consideration must be given to the possible influence of the substrate on the properties of the deposit. Broadly speaking the following criteria should be applied for the selection of the substrate.

1. It should have good conductivity. One can use an insulating substrate, provided a suitably conducting coating is first applied on its surface. Good conductivity of the substrate is also beneficial in improving the carrier collection efficiency.

2. The thermal expansion of the substrate should match well with that of the electrodeposit. Usually, in semiconductor electrodeposition the film requires annealing treatments at temperatures that may be fairly high to improve the grain size or stoichiometry or to fabricate junctions. A mismatch in the thermal expansion often leads to strains that result in cracking or peeling of the film.

3. The substrate should have good mechanical strength.

4. In many applications cost is an important consideration.

5. For epitaxial films, it is necessary to match the lattice parameters between the single crystal substrate and the growing film.

6. The semiconductor metal contacts may be ohmic or rectifying, so care should be given to the type of interface one desires to obtain.

7. In some cases the atoms of the substrates tend to diffuse inside the electrodeposited semiconducting film, especially
during post deposition annealing treatments. The film purity, doping concentration, electronic properties etc., may consequently be altered. Due care should be given to these considerations. The solid solubility, diffusion coefficient and other properties of the substrate atoms in the semiconductor bulk should be examined to avoid such problems.

8. The substrate should be stable in the electrolyte bath.

9. The substrate surface should be smooth and one should avoid surface waviness, porosity, voids, and other irregularities as these influence the local current distribution. Also the electrodeposits tend to reproduce the surface morphology of the substrate. An uneven porous surface with voids will not be useful for any device application.

Subject to the foregoing considerations one may use single crystal, polycrystalline or amorphous substrates of metals or semiconductors in the form of foils, sheets, wafers or thin films. When single crystal semiconductors are used as substrates a back ohmic contact is normally formed by using a conducting paint, a suitable solder or an evaporated film. Metals have been widely used as substrates because of their good conductivity, easy availability, lower cost and relative ease of handling.

3.5.2 Substrate surface preparation

The preparation of smooth scratch free substrate surface is extremely important in semiconductor electrodeposition as surface inhomogeneities tend to amplify during electrodeposition. On the atomic scale surface defects may be point defects, dislocations etc., while on the macroscopic scale they can be scratches left from polishing operations, grain
boundaries etc. Substrate preparation consists of three major steps, grinding and polishing, cleaning and testing the surface cleanliness. Grinding and polishing are usually employed to prepare a smooth surface with a mirror finish. The grinding operation uses abrasives of different grit sizes. Emery paper can be used for grinding, after grinding the surface is either polished mechanically or electrochemically, Mechanical polishing is performed using polishing wheels with abrasive grains glued to them with the help of adhesives or cement compounds. The glues are available in a wide range of viscosities and flexibilities. The abrasive most commonly used in metal polishing is fused alumina grains, which are available in various grain sizes down to 0.3 μm. Fused alumina is hard, sharp, fast cutting and long wearing. Silicon carbide can also be employed for certain special operations. However, it is more difficult to bond it firmly to the wheel. The polishing surface is lubricated with a lubricating oil or grease that can be sprayed or friction applied on to the polishing wheel. Lubrication is desirable to minimize heat and produce a fine polish. Typical speeds of polishing wheels range from 6000 to 8000 revolutions per minute.

In some applications electropolishing can also be employed. This is an electrochemical operation in which the substrate is allowed to dissolve slowly by applying an anodic bias to it. The microscopic projections are dissolved away at a greater rate, resulting in smoothing, leveling and/or deburring. Brightening of the surface takes place simultaneously. The surface brightness achieved by electropolishing is different from that obtained by mechanical means. Electropolishing yields a scratch free, deformation free surface. Time, temperature and current density are the critical parameters that control the surface finish. The surface quality and finish obtained by a prior polishing operation also help to determine the final finish resulting from
electropolishing. One can remove layers of a few micrometers thick using electropolishing.

3.5.3 Cleaning

Surface cleaning in thin film technology is an important step prior to deposition. It is necessary to remove the contaminants that would otherwise affect the properties of the films. The properties that can be affected by the presence of the contaminants include adhesion, morphology, nucleation, electronic properties of the film, and the substrate film interface. The choice of the cleaning procedure is governed by the substrate as well as by the type of contaminants that are likely to be present. The composition, physical properties and chemistry of the substrate should be carefully considered in designing the cleaning operation. The cleaning process should be chosen to avoid any undesirable damage to the substrate surface and yet contaminant is to be removed. It is easier to select the cleaning procedure when the nature and origin of the contaminants are known. Some common contaminants are finger tip grease, glue, dust, leftovers of abrasives, soldering fluxes and similar materials.

3.5.4 Cleaning by solvents

Solvent cleaning is employed to dissolve or emulsify the contamination. Solvent cleaning can be performed by soaking the surface in petroleum or chlorinated solvents. Some common chlorinated solvents are trichloroethylene, methylene chloride, perchloroethylene. These chlorinated solvents may contain hydrochloric acid as a hydrolysis product, and due care should be exercised to inhibit it. Vapor degreasing units are also commonly employed for cleaning. Such a unit consists of a chamber in which a chlorinated solvent is vaporized. Cleaning takes place when the solvent
vapors condense on the colder substrate. Solvent cleaning can also be accomplished by soaking in an emulsifiable solvent. Detergent cleaning is useful for metals. Acid cleaning is often employed to remove oxides and oil from inert glass or metal substrates. An aqueous solution of organic or inorganic acid is normally employed in soaking, painting, brushing or spraying applications. The contaminants are first converted into water soluble compounds that are subsequently removed in a water rinse. Alkaline cleaners along with some surface active agents are often employed after detergent cleaning to remove oil smuts and oxides. Cleaning is generally performed at temperatures of 120 – 200°F. The final cleaning should be done in flowing deionized water.

Ultrasonic cleaning can also be a useful technique, particularly for ceramics. The cleaning is assisted by ultrasonic agitation in which jetting, which accomplishes the collapse of bubbles generated by cavitation near the surface, increases the rate of solvation and emulsification. The cleaning liquid can be water based or solvent based chemical in which the substrates are immersed. The effectiveness of ultrasonic cleaning depends on the intensity of cavitation achieved. Liquids with higher surface tension and lower viscosity should be preferred. The dissolved gases in the liquid also tend to decrease cavitation intensity, whereas increasing temperature increases it. The ultrasonic frequency and power should also be properly chosen. Higher frequencies require more power to maintain the same level and cavitation intensity. Similarly, the ultrasonic power should be matched to the work desired.

3.5.5 Cleaning by Heating

Heating the substrate may remove the volatile impurities. The temperature should be chosen according to the melting point and or surface...
reactivity of the substrate. Heating is not useful if it causes stresses and cracking due to non-uniform heating or oxidation of the surface.

3.5.6 Cleaning by etching

In many cases, a suitable etchant can be used as a clean surface. Etching can be performed in the dark or under illumination. This can be specially used for semiconductor substrates.

3.5.7 Other methods

There are a number of cleaning methods that are more useful than the foregoing for thin film deposition in vacuum system. Three of these methods are sputter cleaning, plasma oxidation and glow discharge cleaning. Cleaning techniques have been discussed by Brown, Holland[51,52].

3.5.8 Surface Cleanliness Test

The various tests that can be applied for checking the surface cleanliness are:

3.5.9 Breath Figure Test

The substrate is brought near the mouth and a soft breath is blown on it. A poorly reflecting black specular film indicates a clean surface. Breath figures of various shapes appear on an uneven surface.

3.5.10 Atomizer Test

Water is sprayed over the surface of the dried substrate. Surface cleanliness is indicated by the formation of fine mist, while on an unclean surface water coalesces into big drops.
3.5.11 Water Break Test

The substrate is pulled against the surface of water in a beaker. If the water sticks to the substrate surface as a continuous film, a clean surface is indicated.

3.5.12 Contact Angle Test

A contact angle zero between water droplet and the substrate implies that the substrate is clean.

3.5.13 Coefficient of friction Test

Resistance encountered when a glass or metal sheet is slid over the substrate can also be a measure of cleanliness. If the coefficient of friction approaches unity the surface is clean.

3.5.14 Indium Adhesion Test

Surface cleanliness is tested by measuring the coefficient of adhesion between the substrate and a piece of indium. It may range from zero for a dirty surface to about two for a clean surface.

3.5.15 Fluorescence Dye Test

Contaminants that can absorb fluorescent dyes can be detected by illuminating the substrate with UV light.
3.5.16 Edge Lighting Effect

It is useful to check transparent substrates such as glass. If the edge of the glass is illuminated, the contaminants present on the surface become visible as lighted areas against a dark background.

In addition to the foregoing techniques one can also employ gravimetric or radiotracer methods.

3.6 ELECTROLYTIC BATH

The electrolytic bath is the medium that supplies the ions that move upon application of an electric field. In general ionic transport is facilitated in aqueous solutions, non aqueous solutions or molten salt bath.

3.6.1 Aqueous and Non-aqueous Electrolytic Solutions

The choice of solvent depends on primary factors such as solubility and non-reactivity.

**Aqueous**: These solvents are suitable for a large number of salts, complexing agents and other compounds. Barring a few hydrolysis reactions, water is generally a nonreactive solvent. However an aqueous solution necessarily contains H$^+$ and OH$^-$ ions, which complicate the electrodeposition process by resulting in the evolution of Hydrogen and / or oxygen at the electrodes.

**Non-aqueous**: These can be further be classified as protic and aprotic solvents.

**Protic Solvents**: (Alcohols, formamide etc.,) These solvents are generally strong hydrogen donors and can exchange protons rapidly. Such solvents also sometimes lead to hydrogen evolution.
**Aprotic Solvents:** They contain hydrogen bonded only with the carbon (propylene carbonate, DMF, DMSO, acetonitrile, tetrahydrofuran etc.).

The nonaqueous solvents have attracted attention for semiconductor electrodeposition work due to the greater flexibility they afford in choosing dopants, solutes, complexants, temperature range and working electrode potentials and the absence of hydrogen evolution reaction, among other reasons.

### 3.6.2 Preparation of Electrolytic Bath

**Selection of Solvent:** The first step is to choose aqueous or non-aqueous solvents depending on the material to be deposited. Electrodeposition solvents are stable in only a limited potential range, beyond which reduction-oxidation take place. This range is called the working potential range or the window. The potential at which the electrodeposition is to be carried out should be within this range. The morphology and rate of growth depends upon the temperature at which electrodeposition is being carried out. The solvent should remain liquid at the desired temperature. Therefore solvents with a large range are preferred to provide greater flexibility.

High vapour pressure solvents are preferred because the electrolytic concentration remains more constant. This is particularly true when the solvent is being purged with nitrogen or an inert gas to drive out the dissolved oxygen.

The dielectric constant should be more than 10. Too low a dielectric constant facilitates ion pair formation, giving poor conductivity and ionization in the solution.
Lower viscosity is always preferred because of the better conductivity and diffusion. Furthermore, many irreversible electrochemical reactions limited by mass transport become reversible in a medium with lower viscosity.

3.6.3 Selection of Supporting Electrolyte

The supporting electrolyte performs several functions in the electrochemical process. (1) It increases the conductivity of the electrolyte. This minimizes Joule heating and provides more uniform current distribution and iR compensation. (2) It reduces the electrode double layer thickness and also influences ion pairing and adsorption. (3) It effectively eliminates the effect of migration in the mass transport. The criteria for selection of a supporting electrolyte are its solubility in the solvent and a dissociation constant sufficiently high to yield good conductivity and the electrochemical oxidation of anion and electroreduction of cation at more anionic or cationic potentials, respectively in the electrochemical process under investigation.

In aqueous media, KCl, HCl have been commonly used. In organic solvents lithium perchlorate, lithium tetrafluoborate, trifluoroacetate and quaternary ammonium salts have been employed as supporting electrolytes.

3.6.4 Additives in Electrolytes

Additives (brightening agents, surfactants, complexants etc.) are often added to the plating bath to obtain a brighter and smoother deposit, controllable reaction rate, better adhesion and also a better texture. The role of additives in the electrodeposition process is used either to control the rate of electrodeposition process or to influence deposit morphology.
3.6.5 Solvent Purity

Impurities in the solvent interfere with the electrochemical processes. In many cases electrodeposition may not be possible or the deposit morphologies may be affected by the impurities. The electronic properties of the semiconductor are also extremely sensitive to impurities that co-deposit. It is therefore essential to purify the solvent. Some of the commonly used methods employ deionization using ion exchange resin or distillation from an alkaline permanganate solution. However this is not a very satisfactory method and many organic contaminants may still be present. Further purification by passing the water vapours through a column of platinum gauge heated to 750 – 800°C in a stream of oxygen is necessary to remove these contaminants. In some case purification by flushing an inert gas to remove oxygen followed by pre-electrolysis at a constant potential may also be employed to remove heavy metal ions.

Non aqueous solvents also need to be purified by refluxing with strong oxidizing or reducing agents, distillation under reduced pressure, or passage through molecular sieves. A common impurity in non-aqueous solvent is oxygen, which can be removed by purging with nitrogen.

3.6.6 Molten Salt Electrolysis Bath

The term molten salt includes molten media that may be wholly ionic or derived from simple salts. The conductivity and ionicity of these systems are generally sensitive to temperature, pressure and composition. Molten salts exhibit a wide range of electrochemical stability high ionic conductivity, high heat capacity and good thermal conductivity. They also exhibit good electrochemical reaction rates. In contrast to aqueous electrodeposition molten salt electrodeposition can be carried out without the
annoying intervention of hydrogen evolution, oxide formation, hydride formation and similar problems.

Some of the commonly used molten salt electrolytes are, NaCl + KCl + Na₃PO₄, NaF + KF + NaPO₃ + In₂O₃, etc. Molten salt baths suffer from certain disadvantages like high operating temperatures, lack of sufficient thermodynamical and kinetic data.

3.7 CLASSIFICATION OF ELECTRODEPOSITION TECHNIQUES

Electrodeposition techniques can be classified according to the nature of the electric field applied across the electrolysis cell:

Deposition at constant dc potential (Potentiostatic)

Deposition at constant dc current (Galvanostatic)

Deposition using a periodic or pulse source.

3.7.1 Potentiostatic Deposition

In this technique different charge transfer reactions proceed under a steady state condition at rates appropriate to the steady state interfacial overpotential and exchange current density. The choice of the overpotential is dictated by the composition of the bath, the substrate and the reversible potential of the species to be deposited. The table of standard electrode potentials serves as an approximate guide in finding the potentials at which electrodeposition of particular species will be possible, but in practice the actual deposition depends on a number of factors such as substrate deposit interaction of the hydrogen overvoltage, the interaction between the components during compound electrodeposition and the polarization characteristics of the bath. Potentiostatic deposition is carried out under pure
activation, diffusion or mixed control depending on the choice of the deposition potential. Potentiostatic deposition has been used to grow layers of elemental, binary and ternary semiconductors. In the case of semiconductors it is desirable to obtain large grained polycrystalline deposits. However, very low overpotential may not be suitable, as they may lead to a spongy or porous deposit due to low nucleation rates. As the overpotential is increased, the supersaturation increases and a large number of nuclei are formed. The deposit thus acquires a fine grained morphology. Very high overpotentials may, however lead to the growth of dendrites or whiskers. In the case of compound semiconductors, more stringent control of the deposition potential is required to maintain the deposit stoichiometry.

3.7.2 Deposition at Constant Direct Current

The constant current between the working and counter electrodes required for electrodeposition at a constant direct current can be obtained from a galvanostat.

The initial guideline for choosing the required deposition current density can be obtained from the knowledge of (1) the Faradaic efficiency and (2) the maximum permissible growth rate for a good crystal. The former can be obtained by a series of preliminary deposition experiments. The latter is to be obtained from the available crystal growth data.

The galvanostatic electrodeposition of compound semiconductors is more complex and a straight forward answer for the proper choice of deposition current density is not possible. As discussed earlier, compound semiconductors are usually deposited by the transport of at least one of the constituents under diffusion control. The simplest situation is when the deposition of all the components is diffusion controlled. The rates of
deposition will then be directly proportional to the corresponding limiting current densities. As an example, consider the cathodic electrodeposition of a binary compound semiconductor $A_x B_y$. If the electrodeposition of $B$ is under diffusion control, then the maximum current distribution due to species $B$ cannot exceed the corresponding limiting current density. Further, if the deposition of $A$ is under pure activation control, then the current distribution due to $A$ for galvanostatic deposition will depend on the value of exchange current density of $A$ and the steady state overpotential. For the compound electrodeposition to be favoured, the value of the total current density should be chosen so that the steady state overpotential satisfies the thermodynamic condition for codeposition of $A$ and $B$.

Galvanostatic electrodeposition is therefore still an art as it depends on the manipulative experience and ability of the individual worker. Initial trials may be necessary to obtain the final optimum values of the electrodeposition current density.

### 3.7.3 Electrodeposition from a Periodic or Pulsed Source

The use of non dc signals for electrodeposition is known to improve the deposit quality. However, only a few reports have appeared on its application to semiconductor electrodeposition. Non-dc electrodeposition can be carried out by either varying the current or the overpotential. Current variation can be accomplished by using a periodic reverse current, a pulsating current or alternating current without or superimposed over a dc current.
3.8 MORPHOLOGY OF THE ELECTRODEPOSITS

The nature and magnitude of the applied electric field across the electrolysis decides (1) grain size (2) surface roughness (3) dendritic growth and (4) spongy and powdery deposit formation.

3.8.1 Grain Size

The grain size depends upon the overpotential which in turn controls whether the deposition is controlled by diffusion, activation or both. The relevant conclusions can be briefly stated as follows. At low overpotentials, initially a small number of nuclei grow independently. It is therefore expected that a large grained deposit will be obtained under these conditions. As the overpotential is increased, a large number of nuclei may be formed leading to a decrease in grain size.

3.8.2 Surface Roughness

At an ideal surface, the value of the diffusion layer thickness and the limiting current are constant throughout, which leads to an uniform growth. Some minor variations in thickness may arise due to convective effect, which is neglected here. However the situation is complex for a real surface which is rough consisting of elevation and recesses. The rate of deposition at the elevations may be higher due to shorter diffusional path between the outer plane of the diffusion layer and the elevations. At the tips of the elevations the diffusion conditions may approach those of spherical diffusion. Spherical diffusion is faster than the linear diffusion because of wider diffusional field in the former case. As a result surface roughness gets amplified during electrodeposition.
3.8.3 Dendritic Growth

In the case of dc electrodeposition, surface roughness can lead to the initiation of preferential growth at protrusions or dendrites. The mechanism of dendritic growth has been studied by Diggle et al and Popov et al [53,54].

3.8.4 Formation of Powdery or Spongy Deposit

Other than dendritic growth another undesirable type of electrodeposit is a powdery or spongy deposit. Dendritic growth is primarily controlled by overpotential or critical current density. However, powdery or spongy growth is interplay of many factors other than the overpotential, such as viscosity and temperature. Powdery deposits are classified by their small particle size and poor adhesion to the electrode surface. They are generally obtained when the deposition is carried out under diffusion limited current conditions or close to transition time. The amorphous nature of the powdery deposit is due to the high nucleation rate. Powder formation is enhanced when the concentration of the depositing species is decreased, the supporting electrolyte concentration is increased, solution viscosity is decreased, the temperature is decreased or the stirring rate is decreased. The mechanism of formation of a spongy deposit has been discussed by Popov et al [55]. It was shown that a spongy deposit is formed if the radius of the growing grain exceeds a critical value.

3.9 SELECTIVE / BRUSH PLATING

An electroplating process performed with hand held portable tool rather than a tank of solution is known as brush plating. The brush plating processes are also called as contact plating, selective plating or swab plating.
This is essentially a plating method, deposition of a metal on the surface by electrochemical means, where the work is connected cathodically to the current source. The plating is then applied by means of a brush or swab, soaked with solution and connected to a flexible anode cable. A direct current power pack drives the electrochemical reaction, depositing the desired metal on the surface of the substrate. In practice, movement between the anode and cathode is required for optimum results when plating, stripping, activating and so on. Currently a broad range of metals can be plated by brush plating. The key advantage of selective plating is portability. Many systems can be moved to various locations in a production facility or be transported to the job site. Selective plating is also versatile since it permits most electroplate types to be deposited onto any conductive substrate that can be touched with an electrode. Cast iron, copper, stainless steel and aluminium can be plated by this method and exhibit good adhesion. Limited adhesion can be obtained with other materials such as titanium, tungsten and tantalum.

Selective plating allows higher current densities than tank plating, which translates into higher deposition rates, upto 0.01 mm/min. In addition, inherently precise thickness control permits plate buildup or repair without the need for subsequent machining.

Besides electroplating, selective plating systems can perform several other ancillary operations:

- Electrostripping for deplating of many metals and alloys
- Anodizing for protecting aluminium alloys
- Electromilling for removing base metal, as in chemical milling
- Electroetching for permanently identifying parts
- Electropolishing for refining a surface chemically
Depending on part size, dimensional considerations and required surface characteristics all of these operations can be done with the same equipment and similar electrodes. Only the solutions are different. In many cases, an operator brush plates only one part at a time. Nevertheless, selective plating is an effective and economical electroplating process when used in application for which it is assigned. These include, plating parts that are too large to immerse in solution, plating a small area of a large component and touching and repair of components, large or small that would cost too much to strip and manufacture. The largest parts ever plated are building domes. The process can also perform at higher production volumes.

Typical selective plating systems include a power pack, plating tools (called as styli or anodes), anode covers, specially formulated plating solutions and any auxiliary equipment required for the particular application. To achieve optimum deposits, equipment should be designed especially for selective plating. Power packs or rectifiers supply the direct current and are specially designed with the features and/or controls required by the process. Output voltage can be typically varied from 0 – 30 V. Voltage control is extremely important because it regulates the current supplied to the process. In turn, the amount of current consumed over time measured in ampere-hour, determines the deposit thickness. A polarity reversing switch allows the operator to automatically change current flow direction, which is necessary in preparatory operations e.g., etching and desmutting and in stripping.

The plating tool stylus must have an insulating handle and an anode material that is inert, insoluble in plating solutions, and able to carry high current. Graphite is by far the most practical choice for anode material. Graphite can be machined or shaped to fit the contour of the part being processed. Stainless steel is much more durable, but it dissolves in certain plating solutions. The anode covers (wrapping materials) serve as an
insulator between the anode and the cathode and help ensure smooth deposits at higher current densities. Anode covers hold the electrolyte; therefore, they must be free of oil and foreign materials. Various fibre like materials make suitable covers. Cotton works very well if it is sterile. Synthetic fibres such as polyester and nylon do not wet or hold electrolytes as well as cotton, but this does not preclude their use. Polyester felts are typically selected when the same anode is used for numerous parts that are to be plated. Most of these materials work well in the form of tube gaze as covers over cotton. Scotch brite has been used when heavy or hard deposits are required and it can also function as a furnishing tool, improving the surface as plating continues. If a surface is soft and easily scratched, a different wrap should be chosen.

3.10 KEY PROCESS PARAMETERS

Controlling continuous movement between the anode and the work piece or cathode, is a key element in obtaining high quality brush plated deposits. However, quality also depends on plating within a specific current density range. The visual appearance of electroplate is also an indicator of quality. A dark grey or black deposit usually corresponds to a burnt deposit, which results from too high current densities or insufficient movement. In contrast, inadequate current density or too much movement produces a generally shiny surface. Anode to cathode movement may be achieved manually or mechanically, such as by using turning equipment to provide a constant rotational speed for cylindrical parts. Another option is a roto-stylus that rotates the anode instead of the work piece.

For the plating process to be efficient, the plating solution must flow between the anode and the area being plated. Solution can also be supplied by periodically dipping the plating tool into the electrolyte. However, the most efficient method is to pump the solution through the block
anode and into the interface between the anode and the work piece. Plating of large areas at high current densities require the use of a pump to re-circulate the solution. This keeps the solution from overheating and results in higher thickness buildup. In addition, the process is faster. The thickness of the deposit can be controlled by monitoring the ampere-hour meter. Each solution has a prescribed energy factor, which indicates how many ampere-hours are required to deposit a given metal thickness on a given area.

In compound semiconductor deposition, however, more than one element is involved and this requires a judicial choice of the concentrations of the precursors for co-deposition of the entities. In the whole world, the first report on semiconductor deposition by brush plating appeared from Central Electrochemical Research Institute (CECRI), Karaikudi, India. Fig.3.1 shows a typical brush plating set up for depositing thin films.

Figure 3.1 Brush Plating Setup