CHAPTER 3

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 and (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, 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 has 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 prereaction 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

\[
  j = j \left[ 1 - \exp \left( \frac{\alpha F n}{RT} \right) \right]
\]

(3.1)
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 increasing 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 \( j_e \). The high efficiency of the cathodic process results from the higher value of \( j_e \). This value can be increased by (1) increasing the concentration \( c^0 \), (2) increasing the diffusion coefficient by working at a higher temperature, and (3) lowering the diffusion layer thickness by forced convection.

### 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 of 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 (Gerischer 1962, Levich 1966, Bockris et al 1973). 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 \( \alpha \) 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., are 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 (Frumkin 1963) gave a detailed account of the role of contact adsorption during 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 50kcal/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 strongly with the electrode surface and $\theta$ become a dominant factor. Apart from solvent adsorption, the role played by the contact adsorbed additives are also significant in controlling $\theta$ (and hence the electrode 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 refer 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 $j_0$ 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
in 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 the 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’s 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, and the resistivity of the semiconductor film can also exercise control 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 CuInSe₂. Unfortunately, the reduction potentials of the nonmetals are widely different from those of the metal ions. The general condition for codepositing 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 most positive value, helping the codeposition.

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 to 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 to 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 electrodeposits. 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 influences 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 0.3μm. Fused alumina is hard, sharp, fast cutting and long wearing. Silicon carbide can also be employed in 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 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 with 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° F to 200° F. The final cleaning should be done in flowing deionized water.

Ultrasonic cleaning can also be a useful technique, particularly in 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 surface reactivity of the substrate. Heating is not useful if it causes stress 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 (Brown 1970, Holland 1955).

3.5.8 Surface Cleanliness Test

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

3.5.8.1 Breath figure test

The substrate is brought near the mouth and a soft breath blows on it. A poorly reflecting black secular film indicates a clean surface. Breath figures of various shapes appear on an uneven surface.
3.5.8.2 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.

3.5.8.3 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.

3.5.8.4 Contact angle test

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

3.5.8.5 Coefficient of friction test

The 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.

3.5.8.6 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 dirt surface to about two for a clean surface.

3.5.8.7 Fluorescence dye test

Contaminants that can absorb fluorescent dyes can be detected by illuminating the substrate with UV light.
3.5.8.8 **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 have become visible as light 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.

#### 3.6.2 **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 $\text{H}^+$ and $\text{OH}^-$ ions, which complicate the electrodeposition process by resulting in the evolution of hydrogen and oxygen at the electrodes.

#### 3.6.3 **Non Aqueous**

These can be further be classified as protic and aprotic solvents.
3.6.4 Protic Solvents

These solvents alcohols, formamide etc., are generally strong hydrogen donors and can exchange protons rapidly. Such solvents also sometimes lead to hydrogen evolution.

3.6.5 Aprotic Solvents

They contain hydrogen bonded only with the carbon (propylene carbonate, DMF, DMSO, acetonitrile, tetrahydrofuran etc.).

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

3.7 PREPARATION OF ELECTROLYTIC BATH

3.7.1 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 takes 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 depend 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 vapor pressure solvents are preferred because the electrolyte 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 becomes reversible in a medium with lower viscosity.

3.7.2 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 the 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.
3.7.3 Additives in Electrolytes

Additives (brightening agents, surfactants, complexes, 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 (1) to control the rate of electrodeposition process or to (2) influence deposit morphology.

3.7.4 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 codeposit. 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 vapors through a column of platinum gauge, heated to 750°C to 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.
3.7.5 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, NaF, KF, NaPO₃, In₂O₃, etc. Molten salt baths suffer from certain disadvantages like high operating temperatures, lack of sufficient thermodynamic and kinetic data.

3.8 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.

3.8.1 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 the 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 a particular species will be possible, but in practice the actual deposition depends on a number of factors such as the 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.

3.8.2 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 straightforward 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 the exchange current density of $A$ and the steady state over potential. For the compound electrodeposition to be favoured, the value of the total current density should be chosen so that the steady state over potential 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.

### 3.8.3 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.
3.9 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.

3.9.1 Grain Size

The grain size depends upon the over potential which in turn controls whether the deposition is controlled by diffusion, activation or both. The relevant conclusions can be briefly stated as follows. As low over potentials, 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 over potential is increased, a large number of nuclei may be formed leading to a decrease in grain size.

3.9.2 Surface Roughness

At an ideal surface, the value of the diffusion layer thickness and the limiting current are constant throughout, which leads to a 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 the shorter divisional 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 get amplified during electrodeposition.
3.9.3 Dendritic Growth

In the case of dc electrodeposition, the 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 1969, Popov et al 1981.

3.9.4 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 over potential or critical current density. However, powdery or spongy growth is an interplay of many factors other than the over potential, 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 transit 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 (Popov et al 1986). It was shown that a spongy deposit is formed if the radius of the growing grain exceeds a critical value.

3.10 BASICS OF PULSE PLATING

Generally in the electrodeposition technique for producing a metal or compound, a driving force (i.e., the free energy) in the form of a potential or current is applied to the electrode. Either of them can be used as a variable as in the case of continuous electrodeposition. Modern electronics allow one
to make use of these parameters as a function of time. This permits a number of possibilities ways of varying the conditions.

Four variable parameters are of primary importance in pulse plating. They are: peak current density, \(i_p\), average current density, \(i_a\), ON time and OFF time. The sum of the ON and OFF times constitutes one pulse cycle. The duty cycle is defined as follows:

\[
\text{Duty Cycle} = \frac{i_p \times \text{duty cycle}}{i_a} \times 100\%
\]  

(3.2)

A duty cycle of 100% corresponds to conventional plating because the OFF time is zero.

In practice, pulse plating usually involves a duty cycle of 5% or greater.

The average current density \(i_a\) under pulse plating conditions is defined as

\[
i_a = \text{peak current density} \times \text{duty cycle} = i_p \times \text{duty cycle}
\]  

(3.3)

During the ON time the concentration of the metal ions to be deposited is reduced within a certain distance from the cathode surface. This so called diffusion layer pulsates with the same frequency as the applied pulse current. Its thickness is also related to \(i_p\) but reaches a limiting value governed primarily by the diffusion coefficient of the metal ions. During the OFF time the concentration of the metal ions builds up again by diffusion from the bulk electrolyte and will reach the equilibrium concentration of the bulk electrolyte if enough time is allowed.
These variables result in two important characteristic features of pulse plating which make it useful for alloy plating as well as property changes as mentioned earlier.

(i) Very high instantaneous current densities and hence very high negative potentials can be reached. The high over potential causes a shift in the ratio of the rates of reactions with different kinetics. This high over potential associated with the high pulse current density greatly influences the nucleation rate because a high energy is available for the formation of new nuclei.

(ii) The second characteristic feature is the influence of the OFF time during which important adsorption and desorption phenomena as well as recrystallization of the deposit occur.