1.1. INTRODUCTION

Electrocrystallisation is the basis for important fields such as corrosion, energy storage and generation, electrodeposition, electronics material development, electrorefining and electrowinning etc. Crystallisation without chemical transformation or charge transfer is the simplest case. In certain instances, the crystallisation is determined by a chemical transformation occurring prior to or simultaneously with the crystallisation process. The part played by the chemical reaction is to supply the material which crystallises. Eg. the crystallisation of barium sulphate by controlled addition of barium ions to a solution containing sulphate ions. Electrocrystallisation is the process which leads to the formation of a new phase (aggregation, clustering or growth) at the electrode/electrolyte interface.

1.1.1. Electrochemical Potential

In the electrocrystallisation process, electrode/electrolyte interface plays a major role [Bockris and Reddy (1970), Newman (1973), Bard and Faulkner (1980), Reiger
Hence, it is necessary to understand the structure of the interface and also influence of this interface on the crystallisation process. At the electrode/electrolyte interface, the rate of charge transfer across the interface is an important factor. If it is very high in both directions, the interface is unpolarizable. If on the other hand, the transfer of electric charge across the interface is hindered, it is polarizable and behaves similar to a capacitor. In this case the potential difference between the two phases is governed by adsorption of ions and dipoles at the interface and the charge required to change this potential difference is relatively small.

The quantity electrochemical potential $\mu_i$ was defined by Guggenheim (1967) for charged species as

$$\tilde{\mu}_i = \mu_i + z_i F \eta$$

where $\mu_i$ is the chemical potential and $z_i F \eta$ is the electrostatic interaction of the particle with the medium.

As like the general crystal growth process in which chemical potential plays the role of driving force, in electrocrystallisation process electrochemical potential is the driving force.

1.1.2. Diffusion

There is always a drift of ions at the electrode/electrolyte interface. This drift of charged
particles occurs by two major processes. If there is a difference in the concentration of ions in different regions of the electrolyte, the resultant concentration gradient produces a flow of ions. This phenomenon is known as diffusion. If there are differences in electrostatic potential at various points in the electrolyte, then the resulting electric field produces a flow of charge in the direction of the field termed as migration or conduction.

When diffusion is occurring, if the driving force $F_D$ and flux $J$ reach values which do not change with time, the system is said to be in steady state. The diffusion flux has been given by Fick's first law as

$$J = -D \frac{dc}{dx}$$

(1.2)

for non-steady state the diffusion relation is given by

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

(1.3)

where $C$ is the concentration of the diffusing species and $D$ is the diffusion coefficient.

1.1.3. Crystallisation Mechanism

Formation of new phase or growth of crystals can take place in a number of situations. The typical conditions are (i) the new phase may be formed on an inert
substrate by electrocrystallisation from ions in solution, (ii) the new phase may be formed from the parent substrate by electrodissolution followed by subsequent precipitation by reaction with the solution. Generally, metals are deposited at potentials negative of their reversible potential termed as overpotential deposition. In certain cases it is possible to deposit a material on a foreign substrate at potentials positive of its reversible Nernst potential, this process is termed as underpotential deposition.

Another interesting way of preparing films is by anodic electrocrystallisation, in which, mostly oxide, halide and sulphide layers are grown on anode. During anodic film formation the parent substrate dissolves into its ions and precipitates after combining with the anions in the solution.

The most important and extensively applied experimental variables for the electrocrystallisation process are potential, current and charge. These variables can be applied to the system in different ways. In potentiostatic method, a constant potential is applied to the system and the current/time response is observed. In potential sweep condition, the potential is linearly varied in a controlled manner and the current response of the electrode system is measured. Galvanostatic method implies,
the application of static current to the electrode system and measurement of the potential response and in coulostatic, charge is passed in a controlled manner and the potential response is measured.

These perturbations can be classified as steady state and transient methods, according to their measurement. For deposition and dissolution studies, the transient method, which involves measurements in a shorter period of time is considered relevant.

So far the various factors influencing the process have been introduced. Now, what will be the nucleus for the electrocrystallisation process has to be identified. The process may be due to nucleation of monomers and spreading by two dimensional or by bulk growth due to three dimensional nucleation. Different nucleation and growth processes have been discussed in part 1.6.

1.1.4. Double Layer

The arrangement of charges and oriented dipoles constituting the interphase region at the boundary of an electrolyte is described as electric double layer or simply double layer [Bockris and Reddy (1970)].

Double layer characteristics can be explained by considering the metal-solution interface (Figure.1.1).
Figure 1.1. Metal-Solution Interface describing the Structure of the Double Layer.

Figure 1.2. Potential drop across the Metal-Solution Interface (Double Layer).
When the metal is charged with an excess charge density \( q_m \), there is either an excess or deficit of free electrons at the surface of the metal. The first layer in the electrolyte is largely occupied by water dipoles. The excess charge on the metal produces a preferential orientation of the water dipoles. The net orientation of the water dipoles varies with the charge on the metal. The second layer in the electrolyte is largely reserved for solvated ions. The locus of centres of these solvated ions is called the Outer Helmholtz Plane (OHP).

Although the first layer in the electrolyte is largely occupied by water molecules there are some ionic species which find their way to the front. The locus of centres of these ions is known as the Inner Helmholtz Plane (IHP). Due to these ionic disturbances, there is a potential drop across the interface as shown in Figure.1.2 and it determines the rate of electrode processes and direction.

The double layer structure at the metal-solution interface has been illustrated by many authors with realistic theories. Perrin, Gouy-Chapman, Stern and Grahame (1947) put forth the principal theories in the subject. The model predicted by Grahame is the latest and stands still. According to him, the dense portion of double layer consists
of two planes namely the inner and outer Helmholtz planes. The inner Helmholtz plane is composed of specifically adsorbed ions, partly or completely dehydrated and forming dipoles with the metal. The outer Helmholtz plane contains hydrated ions drawn to the metal surface by electrostatic forces. Diffuse layer exists between the OHP and the bulk of the solution. Diffuse layer ions penetrate no closer than the outer Helmholtz plane. This model provides a comprehensive interpretation of experimental facts.

1.1.5. Faradaic and non-Faradaic systems

First step in the deposition process is the charge transfer reaction. Let us consider the reversible reaction at the electrode

$$M^{2+} + ze^- \rightleftharpoons M .$$

The corresponding electronation and deelectronation current density can be written as

$$I^+ = zFk_cC_A \exp(-\beta F \Delta \phi_e/RT)$$

$$I^- = zFk_cC_D \exp((1-\beta)F \Delta \phi_e/RT).$$

(1.4)

Where \(z\) is the number of electrons required to reduce the species, \(F\) is the Faraday constant, \(k_c\) and \(k_c^{-1}\) are the forward and backward rate constants, \(C_A\) and \(C_D\) are the concentrations of acceptor and donor species, \(\beta\) is the symmetry factor, \(\phi_e\) is the potential difference across the
interface, \( R \) is the gas constant and \( T \) is the absolute temperature.

1.1.6. Equilibrium Exchange Current Density \( i_0 \)

If external power supply is not connected to the electrode, equilibrium must be reached between the electronation and deelectronation reactions. There must be some value of the potential difference \( \Delta \phi_e \) at which the electronation and deelectronation current become equal \( \dot{i} = \ddot{i} \).

Butler designated such an equilibrium term as the equilibrium exchange current density \( i_0 \) (i.e.)

\[
i_0 = zFkC_A \exp[-\beta zF \Delta \phi_e / RT] = zFkC_D \exp[(1-\beta) zF \Delta \phi_e / RT]. \tag{1.5}
\]

1.1.7. Non-equilibrium Current Density

If the electronation and deelectronation current densities are not equal then there exists a non-equilibrium net current density which is given by

\[
i = \dot{i} - \ddot{i} = zFkC_A \exp[-\beta zF \Delta \phi / RT] - zFkC_D \exp[(1-\beta) zF \Delta \phi / RT] \tag{1.6}
\]

where \( \Delta \phi \) is the non-equilibrium potential difference across the interface (\( \Delta \phi \neq \Delta \phi_e \)). This non-equilibrium potential difference contains two parts, equilibrium potential difference \( \phi_e \) and another part called as overpotential \( \eta \)
by which the potential of the electrode departs from the equilibrium value.

\[ \Delta \phi - \Delta \phi_e = \eta. \]

Now the current density can be written as

\[
i = zF \kappa_c C_A \exp\left[-\beta zF \phi_e / RT\right] \exp\left[-\beta zF \eta / RT\right]
- zF \kappa_c C_D \exp\left[(1-\beta) zF \phi_e / RT\right] \exp\left[(1-\beta) zF \eta / RT\right]
\]

i.e.

\[
i = i_0 \left\{ \exp\left[-\beta zF \eta / RT\right] - \exp\left[(1-\beta) zF \eta / RT\right] \right\}. \tag{1.7}
\]

This is a fundamental equation in electrodics and is called as Butler-Volmer equation [Bockris and Reddy (1970), Bockris and Drazic (1972), Antropov (1972)]. It shows how the current density across metal-solution interface depends on the over-potential(\( \eta \)). Small changes in \( \eta \) produce large changes in \( i \).

### 1.1.8 Nernst Relation

At equilibrium, the individual electronation and deelectronation current densities are equal to the equilibrium exchange current density

\[
i_0 = zF \kappa_c C_A \exp\left[-\beta zF \phi_e / RT\right] = zF \kappa_c C_D \exp\left[(1-\beta) zF \phi_e / RT\right] \tag{1.8}
\]

it follows that

\[
\exp[zF \phi_e / RT] = \frac{[\kappa_c C_A]}{[\kappa_c C_D]}.
\]
Taking logarithms and rearranging,
\[ \phi_e = \frac{RT}{k_C} \ln \frac{zF}{k_C} + \frac{RT}{zF} \ln \frac{C_A}{C_D} . \]

The term \( \frac{RT}{k_C} \ln \frac{zF}{k_C} \)
represents a particular value of \( \phi_e \), when the concentration of electron acceptor to electron donor is standardised to unity. Let it be \( \phi_e^* \).

Now \( \phi_e = \phi_e^* + \frac{RT}{zF} \ln \frac{C_A}{C_D} \)

In a more general case replacing concentration terms into activity terms
\[ \phi_e = \phi_e^* + \frac{RT}{zF} \ln \frac{a_A}{a_D} \quad (1.9) \]

which is the Nerns't equation. And it can be written in a conveniently observable form as

\[ E = E_0 + \frac{RT}{zF} \ln \frac{a_A}{a_D} \quad (1.10) \]

1.1.9. Tafel lines

The Butler-Volmer equation contains two terms namely electronation current density and deelectronation current density. If \( n \) is increased the electronation current
density $i$ decreases and deelectronation current density $i$ increases. When $\eta$ is very high, $i \gg i^*$ and one can neglect $i$.

i.e. $i = i_0 \exp[(1-\beta)zF \eta/RT]$.

Taking logarithm on both sides and rearranging, one gets

$$\eta = -\frac{2.303}{(1-\beta)zF} \log i_0 + \frac{2.303 RT}{(1-\beta)zF} \log i.$$  \hfill (1.11)

When $\eta$ values are plotted at various currents, it is possible to obtain $\eta$ vs $\log i$ plots. Such $\eta$ versus $\log i$ plots are called as Tafel lines. The value of $2.303 RT/(1-\beta)zF$ (Tafel slope) will indicate whether there is a change in the deposition mechanism or not during the deposition process. In some cases it may give information about the way in which molecules are adsorbed on the surface. The intercept $-2.303 \log i_0/(1-\beta)zF$ in the Tafel plot is used to determine equilibrium exchange current density, $i_0$, which is a measure of the rate of the reaction.

1.2. OVERPOTENTIAL

The overpotential, defined as the difference between two electrode potentials, may originate in very different processes [Vetter (1967), Calusaru (1980)]. An overpotential has a specific nature wherever only one reaction or electrochemical process takes place at the
electrode. When several reactions take place at the electrode the potential is mixed. The variation of overpotential with the current density is caused by a hindrance of the process which develops at electrode. If the process consists of several stages the overall reaction must be considered. One of the major steps of any electrochemical reaction is the transfer of charge in the electric double layer, this is a transition reaction and hindrance of this step entails a transition overpotential \( \phi_t \). The charge transfer depends on the electrode potential. The transition overvoltage is the most important for electrochemical kinetics, since it is the only one which depends directly on electrode potential.

Consider the electrochemical process, if one of the partial steps is a chemical reaction, slowing it brings about a reaction overpotential \( \phi_r \) which is no longer influenced by the potential. This has an influence on the total overpotential only when other overpotentials are negligible.

The nature of the chemical reaction, (i.e.) homogeneous or heterogeneous, which is a part of the electrode reaction has to be considered in developing reaction overpotential. In some instances the current may be determined by the rate of chemical electrode reaction, then there exists a limiting current density which is
controlled by the rate of the chemical reaction that hinders the electrode reaction. The reaction overpotential plays a major role when alternating current is used and the equations developed establish that the overpotential depends on the frequency of the alternating current.

In addition to chemical steps with or without mass transfer, transformations and concentration gradients may arise as the electrode reaction advances. In this case the hindrance of electrode process caused a diffusion overpotential $\phi_d$. The sum of diffusion($\phi_d$) and reaction($\phi_r$) overpotentials is called concentration overpotential($\phi_a$).

In the case of crystal deposition, the crystallisation reaction is a characteristic step. It consists of the ordering of atoms formed by the charge transfer within the crystal lattice of the cathode. The hindrance of this reaction is accompanied by crystallisation overpotential. The concept of crystallisation overpotential will exist only when the crystallisation is free from other kinds of overpotential, the discharge and transport, as well as chemical reactions are very close to thermodynamic equilibrium even under dynamic conditions (current flowing across the interface).
1.3. ELECTROCHEMICAL REACTIONS

An electrochemical reaction has been defined as a reaction in which both chemical bodies (neutral molecules and/or ions) and free electric charges or electrons $e^-$, participate.

Typical of electrochemical reactions are the decomposition of water, synthesis of water, corrosion of metals etc. These electrochemical reactions are oxidation-reduction reactions which proceed in the direction of an oxidation if they correspond to a liberation of negative electric charge and in the direction of a reduction if they correspond to a consumption of negative electric charge.

Consider a given electrochemical reaction proceeding at the interface between a metal and an aqueous solution, independent of the fact that this reaction is associated with one or more other electrochemical reactions. The potential difference measured between this electrode and a reversible reference electrode is called the electrode potential $E_1$ of this electrode. In the particular case where this corresponds to the state of equilibrium of the electrochemical reaction proceeding on this electrode it is called the equilibrium potential of the reaction $E_0$. When all the constituents of the reaction are in a standard state (activity $\text{lg-molecule/lit}$) or $\text{lg-ion/lit}$ for dissolved
bodies, fugacity of 1 atm for gaseous bodies) then the
equilibrium potential is the standard equilibrium potential
$E^\circ_0$ of the reaction.

The equilibrium potential increases when the
activity of the oxidised form increases and it decreases
when the activity of the reduced form increases.

1.3.1. Graphical Representation of Electrochemical Equilibria

Consider the electrochemical reactions in which
water dissociates into $H^+$ ions and $OH^-$ ions, accordingly

$$\begin{align*}
2H^+ + 2e^- & \rightleftharpoons H_2 & \text{reduction} \quad (a) \\
2H_2O & \longrightarrow O_2 + 4H^+ + 4e^- & \text{oxidation} \quad (b)
\end{align*}$$

$$\begin{align*}
E_a^\circ &= 0.000 - 0.0591 \text{pH} - 0.0295 \log P_{H_2}^2 \\
E_b^\circ &= 1.228 - 0.0591 \text{pH} + 0.0147 \log P_{O_2}^2
\end{align*}$$

If $P_{H_2}$ and $P_{O_2}$ are 1 atm,

$$\begin{align*}
E_a &= 0.000 - 0.0591 \text{pH} \\
E_b &= 1.228 - 0.0591 \text{pH}
\end{align*}$$

These two conditions of equilibrium are represented
in a diagram where the pH is plotted horizontally and the
potential vertically as parallel lines (a) and (b) of slope
-0.0591. Between these two lines the equilibrium pressures
of $H_2$ and $O_2$ are both less than 1 atm, the region between
these two lines then is the area of thermodynamic stability of water under a pressure of 1 atm.

Below the line 'a' corresponding to \( P_{H_2} = 1 \text{ atm} \), water under a pressure of hydrogen of 1 atm will tend to decompose by reduction according to the reaction

\[
2H^+ + 2e^- \rightarrow H_2.
\]

Above the line 'b' corresponding to \( P_{O_2} = 1 \text{ atm} \), water under a pressure of oxygen of 1 atm tends to decompose by oxidation according to the reaction

\[
2H_2O \rightarrow O_2 + 4H^+ + 4e^-.
\]

When the equilibrium conditions do not depend on pH but depend on the electrode potential, they are represented by a family of horizontal lines each of which corresponds to a definite value of logarithm of the function of pressures and/or concentrations in the potential-pH diagram.

When the equilibrium conditions depend both on the pH and the electrode potential, they are represented by a family of oblique parallel lines each of which corresponds to specific value of the logarithm of the function of pressure and/or of concentration in the potential-pH diagram.

When no gaseous or dissolved bodies other than the \( H^+ \) ion take part in the reaction, these family of lines
reduce to a single line of slope -0.0591. For an electrochemical reaction likely to be produced in a given system, this diagram of electrochemical equilibria makes it possible to represent the circumstances in which each of these given bodies is thermodynamically stable or unstable regardless of the complexity of the given system.

1.3.2. Establishment of the diagram

Consider the system copper, its oxides and hydroxides in aqueous solution, free from substances that form soluble complexes or insoluble salts with copper.

To establish equilibrium diagrams, the influence of pH and electrode potential on the equilibrium characteristics of the various possible reactions in which copper, its oxides and hydroxides are participating is determined. Then it is possible to define in the reaction equation, the H⁺ ions and the electric charges e⁻ involved in the reaction. The equilibrium conditions of homogeneous reactions in aqueous solution relative to copper, which indicate the conditions of relative stability of the dissolved forms and the heterogeneous reactions, which indicate the conditions of relative stability of the solid bodies in the system are separately derived and the diagram is drawn superimposing one over the other.
The potential-pH diagrams will define regions where copper is soluble notably as $\text{Cu}^{2+}$, $\text{HCuO}_2^-$ or $\text{CuO}_2^{2-}$ ions and where it exists as condensed phases such as the pure metal or compounds. If the pH and potential are such that the metal environment system exists in a region where Cu$^{2+}$ is stable, then copper may dissolve until an equilibrium Cu$^{2+}$ concentration is attained. This dissolution is simply corrosion. Thus, while the metal environment system exists in the region of soluble ions, it may be expected to corrode. If, on the other hand it exists in the region of potential and pH where the metal is stable (the more negative direction of potential) then the metal will not corrode or will be immune from corroding. If the metal environment system exists in a potential-pH region where a solid product e.g. Cu$_2$O is stable, then the corrosion rate may be expected to be minimal because of a covering by this solid product. Such a regime is called a region of passivation, which denotes, an action toward passivity. When the metal exists in the region of passivation, for solutions not containing chlorides, oxide films are generally perfectly protective for aluminium, chromium, iron and tin, they are generally not protective for copper. A metal will be considered more noble as the region of immunity lies more within the region of stability of water. These potential-pH diagrams are called Pourbaix diagrams [Pourbaix (1973)]. The noble nature of the
materials can be altered in the presence of complexing agents and other salts in the solution medium.

1.4. EXPERIMENTAL OBSERVATIONS

Many real observations have been made on solid surfaces having screw dislocations, steps, etc. Nucleation phenomenon was observed on defect free surfaces. Budevski and his co-workers [Budevski (1982), Bostanov et al (1981)] using a simple and elegant method showed that, on dislocation free (100) face of silver, a potentiostatic pulse with suitable amplitude and duration (e.g. 12 mV, 100 µsec) led to the formation of just one two-dimensional nucleus. Such lone centre experiments have greatly aided in testing the two dimensional nucleation and growth mechanisms. Usually nucleation takes place on a large number of centers scattered randomly throughout the surface. For potentiostatic work on these surfaces the transients [Bostanov et al (1975)] as shown in Figure 1.3. are observed. Which have initial fall, shoulder, minimum etc. and are explained by adsorption mechanisms and by under potential deposition process [Bewick and Thomas (1975), Schultze and Dickertmann (1976), Pereira and Peter (1981), Hilbert et al (1973), Lorenz et al (1974)].
Figure 1.3. Typical potentiostatic transients observed in Electrochemical Phase Formation
(a) Nucleation and Growth, (b) Anodic Oxidation, (c) Underpotential deposition
of Pb on Ag(111) and (d) Underpotential deposition of Pb on Cu(111).
Experimental observation of 3D growth [Nabarro and Jackson (1958), Peter et al (1981), Mathews et al (1961)] from anodic film formation, in the growth of HgO on Hg and transient measurements in the systems Pt/α-PbO₂ and Pt/γ-MnO₂ indicate macrogrowth which reaches either a steady state (Figure 1.4) [Fleishmann (1962)] or passivation (Figure 1.5) [Armstrong (1966)].

Bostanov et al [1972] observed multilayers of silver spreading across silver single crystal surface. Current oscillations and a steady state were noticed in the potentiostatic response of electrocrystallisation of Ag on dislocation free cubic planes (Figure 1.6).

In the electrocrystallisation of nickel the potentiostatic transient exhibits a maximum before attaining a steady state (Figure 1.7) [Abyaneh and Fleishmann (1981)]. In the electrolytic nucleation of mercury on graphite, the current has a maximum which is followed by 1/t¹/² fall (Figure 1.8) due to diffusion.

High resolution microscopic techniques such as SEM, TEM are used to determine the nuclear number densities. Palmisano studied the potentiostatic deposition of Pb on glossy carbon electrodes in combination with SEM. Jacobs [1988] studied the potentiostatic current transient for photoelectrochemical deposition of Au on p-type GaAs using
Figure 1.4. The Formation of HgO in 5 M NaOH. Overpotential 25 mV.

Figure 1.5. Current-time transient for the deposition of $\alpha$-MnO$_2$ on Pt.
Figure 1.6. Oscillation of the Current during electrocrystallisation of silver, indicating a multilayer mechanism of deposition.

Figure 1.7. Current-time transient for the deposition of Nickel on a vitreous Carbon electrode at -0.90 V (SCE).
Figure 1.8. Transient corresponding to a constant Growth rate and Instantaneous Nucleation.
electron microscopy and reported that Au deposition is characterised by three dimensional progressive nucleation and growth of Au clusters followed by diffusion controlled growth and coalescence of Au particles. Mirkin and Nilov [1990] studied the potentiostatic transient for electrodeposition of Antimony on mercury. In all cases, the calculated values of nuclear density were orders of magnitude smaller than directly observed densities. This discrepancy has been attributed to the following facts.

1. The assumption of each individual nucleus having hemispherical diffusion zones on the plane of the electrode, leading to large diffusion fields and low nuclear number densities.

2. Not considering the presence of 'exclusion zones' around growing nuclei within which the nucleation process is either slow or does not take place.

3. Neglecting the effect of the substrate effects such as metallic nature (metal, semiconductor, etc.), surface property (clean, porous, size) and interaction with the system.

4. The neglect of the concentration dependence of the nucleation rate and
5. The neglect of the Thomson effect and the dependence of growth rate of nuclei on the size of the nucleus and nucleus-substrate interaction.

These experimentally observed facts have been studied and explained with the models proposed by several authors. The details of the models are explained later.

1.5. PHENOMENOLOGICAL CONCEPTS AND TECHNIQUES

The first step in the electrochemical phase formation is the nucleation phenomenon. The surface of the solid metal electrode has a complex character, with different crystallographic orientations and inter grain boundary regions. In addition, crystal defects, inclusions, adsorbed molecules, oxide layers complicate the nature of the surface. The simplest conditions are the inert electrodes and single crystals.

In the electrocrystallisation process, discrete nuclei have been found to form, usually at preferred sites. If there is a uniform probability, the conversion of sites into nuclei with time is given by the nucleation law as [Greef et al (1985), Fleishmann and Thirsk (1963)]

\[ N = N_0[1 - \exp(-At)] \]  \hspace{1cm} (1.13)

where \( N_0 \) is the total number of sites and \( A \) is the nucleation rate constant.
If $A$ is large, all the sites are converted instantaneously

$$N = N_0$$  \hspace{1cm} (1.14)

while if $A$ is small, nucleation progresses with time as

$$N = AN_0t.$$  \hspace{1cm} (1.15)

1.5.1. Crystallisation on a Single crystal

A perfect defect free crystal is bound by singular faces, hence it exhibits no sites for growth. The only way for further growth is the formation of two-dimensional clusters of adatoms giving birth to a new lattice net, which with its peripheral step, would make atom incorporation into the crystal lattice possible. So 2D nucleation process is required for the deposition of every new layer. This is because one atom deposited on the crystal face has a smaller bond energy to the crystal than a kink atom and it stays only temporarily on the surface as an adatom. A very important factor is the tendency of these surface atoms to cluster together thereby increasing their stability. Clusters of that kind are potential nuclei of a new lattice net.

Using the classical Gibbs equation, the free energy of formation of a cluster consisting of $N$ atoms is

$$\Delta G(N) = -Nze_0\phi_C + \phi(N)$$  \hspace{1cm} (1.16)
where $N$—the size of the cluster, $\phi_c$ the cathodic overpotential, $e_0$—charge of the electron and $\phi(N)$ is the surface energy.

The first term accounts for the transfer of the $N$ atoms across the double layer at the cathodic overpotential and the second term for the increase of the surface energy. The only change in the surface energy during the formation of a 2D cluster on a substrate of the like metal is the energy connected with the formation of the peripheral edge of the cluster. Then $\phi(N) = uP$, where $P$—is the perimeter of the cluster and $u$, the specific periphery or edge energy. In the anisotropic case, where $u$ depends on orientation the cluster has a polygonised form and $\phi(N)$ is given by $\phi(N) = \sum u_i L_i$ where $L_i$ is the length of the $i$th side of the polygon.

As the periphery energy $\phi(N) = uP$ increases with $N^{1/2}$, the first term is linear in $N$, the value of $G(N)$ after an initial rise passes through a maximum and becomes negative only for sufficiently large clusters. The maximum of $G(N)$ corresponds to the size of the critical nucleus. The size as well as the free energy of formation of this critical cluster [Budevski (1982)] is

$$N^* = b s u^2 / (z e_0 \phi_c)^2$$

$$\Delta G^* = b s u^2 / z e_0 \phi_c$$

(1.17)
where \( b \) is the factor relating the surface area \( S \) of the nucleus to its perimeter \( P = \Sigma L_i \), \( s \) is the area occupied by one atom on the surface of the nucleus. When the geometrical form of the nucleus is a circle or a regular polygon, the size can be given by the radius \( \rho \) as

\[
\rho^* = \frac{s\nu}{\varepsilon_0 \phi_C}.
\]  

(1.18)

Here, the constant \( \varepsilon_0/s \) can be replaced by its equality \( q_{\text{mon}} \) giving the amount of electricity per unit area needed for the deposition of one monoatomic layer. Then

\[
\rho^* = \frac{\upsilon}{q_{\text{mon}} \phi_C}.
\]  

(1.19)

The rate of 2D nucleation (i.e.) the rate of formation of clusters big enough for spontaneous growth is proportional to the population of critical nuclei and is given by

\[
J = k_1 \exp\left(-\frac{\Delta G^*}{kT}\right) = k_1 \exp\left(-\frac{b\upsilon^2}{q_{\text{mon}} kT \phi_C}\right)
\]  

(1.20)

where \( k_1 \) is the preexponential term defined by \( k_1 = n_0 \Gamma w^* \), \( \Gamma \) is Zeldovich non equilibrium factor and \( \Gamma = \left(\frac{\Delta G^*}{3\pi kTN^*^2}\right)^{1/2}, \) \( w^* \) is the probability for an adatom to join the critical nucleus, \( n_0 \) is the surface atomic density. \( \Gamma \) and \( w^* \) are weakly dependent on overpotential and are usually considered constants. The \( J-\phi_C \) relationship shows a sharp rise of the nucleation rate at a critical value below which the rate is negligibly small. The existence of a supersaturation or overpotential threshold in the growth of
A crystalline phase is a very characteristic feature of nucleation induced processes.

Budevski (1982) investigated the 2D nucleation kinetics on screw dislocation free faces. The propagation technique of dislocation free faces of silver single crystals utilised by Budevski is as follows. An appropriately oriented single crystal is enclosed in a glass tube with a capillary ending and is used as a cathode in an electrolytic cell. The seed crystal is grown electrolytically into the capillary ending of the tube. Using an ac superimposed on the cathodic current, the front face can be grown as a perfect, dislocation free face, filling the whole cross section of the capillary usually of about 0.2 mm diameter. The nucleation overpotential threshold for the formation of nuclei has been determined for each of the source materials, and the current value following the overpotential is observed. When an overpotential pulse exceeding the threshold value is applied, a current following this pulse shows that one or more nuclei have been formed. The nucleation pulse can be adjusted in amplitude and duration in such a way that a nucleus will be formed during the half pulse duration. Then the pulse duration is considered as the time lapse needed for the single nucleus with 50% probability. The time lapse can be determined at different overpotentials.
relation connecting the nucleation rate and the reciprocal of the overpotential is arrived. The relation between these two quantities is linear. The contribution of the overpotential dependence of the Zeldovich factor and the attachment frequency are small enough to produce appreciable effect on this relation. The frequency factor $K=n_0w_C$ in the rate equation and the specific edge energy $\bar{u}$ can be calculated from the intercept and slope of the $\ln J - 1/\theta_C$ curve.

In certain cases, 2D nucleation and growth will be influenced by active centres, then nucleus formation can proceed instantaneously from the beginning of the pulse.

On dislocation free faces, the instantaneous nucleation has been studied by Budevski. For this purpose, a nucleation pulse is applied to the dislocation free face prepolarised at a growth overpotential $\phi_C < 5$ mV. The nuclei created during the nucleation pulse are grown at the lower overpotential of growth and the current transient is recorded. From the transient $N_\sigma$ and $J=N_\sigma/\tau$ are obtained. And, $\ln J$ vs $1/\phi_C$ relation is analysed at different overpotentials, from which the edge energy has been determined.
1.5.2. Layer Growth

Layer growth is not equivalent to growth of ideal crystals, which consist of planes of atomic dimension. The layer structure is a growth in which lattice defects play a determining role. The nucleation and spreading of each of the layer over the face fluctuates the current due to the development and decay of the peripheral edge of each monolayer. Now, the mean current density is given by

\[ i = \frac{1}{\tau_n} \int_{\tau_n}^{t_n} i(t) dt = J_{sq_{mon}}. \] (1.21)

Thus current density depends on nucleation frequency and is independent of rate of propagation.

In the initial stage, the plane is completely intact and does not expose sites for growth. When the current is switched on, the overpotential rises rapidly making way for the multi nucleation process. The kinetics of formation of monoatomic layer on an intact face is given by Budevski as

\[ i = q_{mon} bJV^2 t^2 \exp(-bJV^2 t^3/3). \] (1.22)

The preexponential term gives the current flowing due to independently growing nuclei and the exponential term gives the overlap effect. The current time transient obtained for a (100) face of a silver single crystal is linear. From the slopes of series of curves recorded at
different overpotentials, the value of $Jv^2$ as a function of $\phi$ can be obtained. Then $\ln J$ vs $1/\phi$ analysis has been made. From which the value of $\dot{\phi}$ was found from the time lag in formation of a single nucleus.

1.5.3. Multinuclear Multilayer deposition

At high current densities the overpotential remains for a relatively longer period at a high value and more than one nucleus can be formed. As nucleation proceeds continuously, new nuclei are formed on top of the deposited first layer long before it had covered the whole area of the surface. The same happens with the third, fourth and so on layers. The multilayer surface structure determines a dying away of the initial oscillations and a steady state is reached. The deposition process under these conditions are called Multinuclear Multilayer deposition. The theory discusses the growth of a series of parallel, equidistant monoatomic steps on the basis of two mechanisms, the surface diffusion mechanism and the direct transfer mechanism. In both cases, at low overvoltages $\phi \ll RT/zF$, assuming the depth of surface diffusion penetration $\lambda_o$ is smaller than the step spacing $2x_o$, the current density is linearly dependent on the overvoltage and step length given by $i=k'L_s\phi$ where $k'$ is the kinetic constant given by $k=2ia\lambda o^2F/RT$ for surface diffusion and $k=2i_s^2zF/RT$ for direct transfer and $L_s$ is the step density. In these
expressions $i_a$ and $i_s$ are the exchange current densities of the adatoms and atoms of the monoatomic step with the metal ions in the bulk of the electrolyte respectively, and $\delta$ is the width of an atom row added to the edge of the step. The theory of crystal growth assumes that the building up of each new monoatomic layer on a perfect crystal face involves the appearance of only one two dimensional nucleus which propagates on the whole surface $S$ of the face. For this growth mechanism the period between the two acts of nucleation $r_k = 1/JS$ should be several times greater than the time $r_a = S^{1/2}v^{-1}$ necessary for the nucleus to cover the entire face. In the reverse case, inequality $r_k << r_a$ is valid, in which the crystal face will grow by the so called multinuclear multilayer growth mechanism.

A three dimensional nucleation/growth process includes many stages: diffusion of ions to the electrode, discharge on its surface with resulting adatoms, critical nuclei formation, crystal growth and overlap as a result of diffusion and ion discharge on the crystal surface and also the arrangement of adatoms into a crystal lattice. The rate of nucleus formation $J$ can be stated in terms of the inverted Boltzmann statistical formula for the entropy. The three dimensional nuclei also can be formed only as the result of statistical fluctuation phenomena involving transient local decreases in entropy.
1.5.4. Overlap

The phase formation involves not one centre but many which nucleate, grow and impinge on each other. Growth may stop at the points of collision, the collided clusters coalesce (e.g. Hg) to form one bigger mass or they may even repel each other. Overlap is the interesting part introduced in growth forms [Bewick et al (1962), Bosco and Rangarajan (1981)].

Fundamental formula for overlap is given by Avrami [(1939), (1940), (1941)] as

\[ S = 1 - \exp (-S_X) \] (1.23)

where \( S \) is the true coverage and \( S_X \) is the sum of the lone centre coverages ignoring overlap.

In Evans approach, he considered a representative point \( P \) and determined the probability \( P_n(t) \) that \( n \) nuclei would have grown upto the point \( P \) and occupied it in time \( t \) (i.e.)

\[ P_n(t) = E_C(t)^n \exp \left(-E_C(t)\right)/n! \] (1.24)

where \( E_C \) is the average number of nuclei whose peripheries had crossed \( P \) by time \( t \). \( P_0(t) \) has a special significance in that it is a measure of the vacant surface area. So

\[ P_0(t) = 1 - S \]

and

\[ S = 1 - \exp(-E_C(t)). \] (1.25)
1.5.5. **Polarography**

Polarography is an electroanalytical technique in which both the current flowing in the circuit and the potential being applied to the electrodes are measured simultaneously. The electrode at which deposition takes place has to be small in size so that it can become completely polarised and it should not alter in nature during analysis. Though the polarising electrode may be in any form, usually mercury electrodes are used for this purpose.

Current voltage curves are ideally perfect S-shaped curves. The magnitude of the current becomes proportional to the amount of reducible species present if conditions are adjusted so that the ions reach the cathode by a diffusion process only. The polarographic diffusion current is described mathematically by the Ilkovic equation as

\[ i_D = 706 \frac{n C D^{1/2} u^{2/3} t^{1/6}}{} \]  

(1.26)

where \( n \) is the number of Faradays of electricity required per mole of the electrode reaction, \( D \) is the diffusion coefficient of the reducible substance, \( u \) is the rate of flow of mercury from the dropping electrode and \( t \) is the drop time. This equation predicts that the diffusion current \( (i_D) \) will be directly proportional to the concentration of reducible species in the solution \( (C) \).
provided that D, u and t remain constant. The magnitude of the diffusion coefficient varies from species to species and it is common practice to determine the diffusion currents of solutions containing known concentrations of the reducible species and these currents are then plotted against concentration to yield a calibration graph.

Polarography is used to study any reaction that involves electron transfer, for the determination of inorganic ions and organic compounds and to study oxidation and reduction processes, electrode phenomena, stability and structure of complexes, reaction rates, etc. Under ideal conditions, four or more species may be determined from a single polarogram and more than one determination may be achieved on a single polarogram.

1.5.5. Voltammetry

The current potential curve for an electrochemical reaction obtained with electrodes, other than dropping or static mercury electrode are called voltammograms. The study of different types of voltammograms is voltammetry.

1.5.6. Linear Sweep Voltammetry

The current potential curve obtained by varying the potential linearly with time is called linear potential sweep voltammogram or peak polarogram.
Consider a negative going potential sweep, when the reduction potential of species 0 is reached the current rises sharply as 0 near the electrode surface is reduced, the current then becomes diffusion controlled and begins to fall. When the potential is well past the half-wave potential, the current falls as $t^{-1/2}$.

The peak current for a reversible process at a planar electrode is found to be

$$i_p = 0.446nFA (nF\mu/RT)^{1/2}D^{1/2}C^{1/2}$$

(1.27)

where $\mu$ is the potential scan rate in V/sec. For a reversible process, the shape of the curve and the peak potential are independent of scan rate, but the peak current is proportional to $\mu^{1/2}$. The capacitive charging current produced due to changing potential and the ohmic potential drop in the solution due to large peak current are the two factors which reduce the accuracy of this method.

1.5.7. Cyclic Voltammetry

Instead of a linear potential variation, if a triangular wave potential is applied to the cell, the indicator electrode potential is swept linearly through the voltammetric wave and then back again. On the forward scan, the current response is just the linear potential sweep voltammogram as 0 is reduced to R. On the reverse scan, the
R molecules near the electrode are reoxidised to O and an anodic peak results. The resulting curve is called a triangular wave cyclic voltammogram.

If the initial scan is carried far beyond the cathodic peak so that the diffusion layer is very thick and the cathodic current has decayed nearly to zero, then the concentration of R at the electrode surface is equal to C. Thus the amount of R available for oxidation on the reverse scan is the same as the O available on the forward scan and the current peak has the same shape and the magnitude as on the forward scan, but reflected at \(E = E_{1/2} \) and changed in sign.

When the switching potential is less negative such that the cathodic current is still significant at the switching point, the diffusion layer is thinner, the R concentration falls to zero more rapidly with distance from the electrode, and the resulting anodic peak is smaller. However, it turns out that, if the anodic peak current is measured from a baseline equal to the cathodic current which would have flowed at the time of the anodic peak had the potential scan continued in the negative direction, then the anodic to cathodic peak current ratio is exactly 1.

The response on the second and subsequent cycles of a cyclic voltammogram is qualitatively similar to that of the first cycle but with current peaks somewhat reduced in
amplitude. The reason for this decrease is that the concentration profiles of 0 and R do not return to initial conditions at the completion of a cycle. On multiple cycles, a steady state is eventually reached with damped concentration waves propagating out into the solution.

1.6. ELECTROCRYSTALLISATION - MODELS
1.6.1. Nucleation - growth model

Electrocrystallisation process can be explained by considering the nucleation growth model. This model visualises two or three dimensional nuclei activation and growing, aided by electrochemical reactions. This model considers three basic features, (i) presence of growth centres or nuclei whose activation is a precursor to their growth, (ii) the growth of such activated centres is aided by electron transfer at the kink sites available at the peripheries of the centres and (iii) there is overlap (ie) there is centre centre interaction in the multi centre growth.

At the atomistic level, growth of a lone centre must strictly be modelled as an asymptotic limit of atomic edge by edge growth at the periphery of the growing centre [Rangarajan (1973 a)].
The rate of nucleation in general form is

\[ \frac{dN}{dt} = N_0 A(n) \exp\left(-\int A[n(\tau)]d\tau\right) \]  \hspace{1cm} (1.28)

where \( N \) is the number of nuclei, \( N_0 \) is the number of active centres, \( A(n) \) is the nucleation rate and \( n \) the overpotential.

The surface coverage is given by

\[ S = 1 - \exp(-S_x) \]

where

\[ S_x = \int_0^t \int_0^t \frac{dR}{dz} \left( \frac{dz}{dy} \right)^2 \frac{dN}{dt} \frac{dy}{dt} \]

\( R_0 \) is the radius of the lone growing centre and \( g \) is the geometrical factor.

The current expressions are [Greef et al (1985), Bosco and Rangarajan (1981)]

\[ i(t) = 2q_m g N_0 (r \bar{u} K)^2 t \exp[-g N_0 (r \bar{u} K t)^2] \] \hspace{1cm} (1.29)

for instantaneous nucleation and

\[ i(t) = q_m g N_0 A(r \bar{u} K)^2 t^2 \exp[-g A N_0 (r \bar{u} K)^2 t^3/3] \] \hspace{1cm} (1.30)

for progressive nucleation.

Where \( r \) is the proportionality constant, \( \bar{u} \) is the edge energy and \( K \) is the electron transfer rate.
1.6.2. Macrogrowth

The study of macrogrowth on surfaces will lead to understanding the phenomena like passivation, formation of whiskers, dendrites and stability of interfacial structures.

A natural extension of the monolayer growth to describe the bulk phenomena are the multilayer model. Monolayer can serve as the basis for multilayer formations through 2D nucleation, growth and overlap.

The problem was well studied [Vetter (1967), Armstrong and Harrison (1969), Bertocci (1969), Harrison and Rangarajan (1971), Gilmer (1977) and the exact steady state expressions were given [Rangarajan (1973 a,b)] confirming the basic features.

In the cascade model, the (n+1)th layer is assumed to be born on the nth layer by 2D nucleation and growth. The fraction of the total area covered by the nth layer in the time interval \( r \) to \( r + dr \), viz. \( dS_n(r) \), becomes overlaid in the time \( r \) to \( t \) by the fraction \( 1 - \exp \left[-S_{x,n+1}(t,r)\right] \) of the (n+1)th lattice layer. Now, the general expression for current is given by

\[
\begin{align*}
I_{n+1}(t) &= \int_0^t f_n(t-\tau) i_n(\tau) d\tau \\
I_O(t) &= \delta(t) \quad (1.31)
\end{align*}
\]

where \( \delta(t) \) is the Dirac delta function.
A passivation model was considered where the vertical growth rate was a decaying function of time.

\[ V_2 = V_{20} \exp\left(\frac{-\pi M^2 k_1^2 At^3}{3p^2}\right) \]

The horizontal growth rate was constant and the nucleation was progressive. Now, the expression for current is

\[ i = z F k_2 \left[ 1 - \exp\left(\frac{-\pi M^2 k_1^2 At^3}{3p^2}\right) \right] \exp\left(\frac{-\pi M^2 k_1^2 At^3}{3p^2}\right), \]  

where \( k_1 \) and \( k_2 \) are the nucleation-growth rates, \( M \) molecular weight and \( p \) the density. This passivation model will be very much utilised for corrosion prevention phenomena. The above equation is found to have shortcomings and have been suitably modified [Bosco and Rangarajan (1982)] as

\[ \frac{ds}{dt} = q_0 \int_0^t ds \exp\left( -\chi s^3 - S_{x,s,t}\right) \frac{dS_{x,s,t}}{dt} + q_0 \exp(-\chi t^3) \left[ 1 - \exp\left(-N_0 AV_2^2 t^3/3\right) \right] \]

where \( \chi \) is a proportionality constant.

1.6.3. Two Rate Model

In the two rate model [Armstrong et al (1966), Kolb et al (1977), Barradas et al (1977), Fletcher and Mathew (1981), Bosco and Rangarajan (1982 a)], two growth rates, one vertical and the other horizontal were
postulated. Here the vertical growth is nucleation like and the horizontal growth is by 2D layer formation. Though, this model has layer by layer 2D nucleation, 2D growth and overlap like the cascade model, the nucleation centres are restricted and are not random.

The general expressions for extended coverage and current are given by [Bosco and Rangarajan (1982 a)]

\[ S(h,t) = g \int_0^h dN \frac{d\tau}{dt} \int P(u) du \]

\[ S(h) = 1 - \exp(-S_{x,h}) \]

\[ S = \int_0^t gh \, dh \]

\[ hm = \int q(u) du \]

where \( h \) is the height, \( t \)-time and \( dN/dt \) is the rate of nucleation on the substrate.

Now,

\[ i = \frac{zFp}{M} \frac{ds}{dt} \]  (1.35)

The macrogrowth can be controlled by either electron transfer or diffusion. For potentiostatic observation,

Nucleation rate = constant (electron transfer)

\[ \propto \frac{1}{t^{1/2}} \] (diffusion)

\[ \propto \exp(-\beta t^h) \] (substrate aided growth)
1.6.4. Underpotential Deposition

The presence of nucleation in the UPD of thallium and lead on Ag single crystals and Pb on Cu(111) have been reported by Bewick [1975]. The potentiostatic transients in these systems reveal the familiar nucleation growth forms. Progressive nucleation was inferred in Pb/Ag (110) from (Equation 1.30) $\log(i/t^2)$ vs $t^3$ plot. Instantaneous nucleation was inferred in Pd/Cu (111) from (Equation 1.29) $\log(i/t)$ vs $t^2$ plot. In all these cases there is a marked deviation from the straight line in the small time region, which reflects the initial fall/shoulder in the corresponding potentiostatic transients.

1.6.5. Anodic Film Formation

Monolayer nucleation growth models have been applied to the formation of many anodic films: Calomel on mercury, mercuric sulphide on mercury, CdOH and TlCl on the respective metal amalgam surfaces, ZnO on Zn amalgam and oxidation of PbSO$_4$ to PbO etc. In the potentiostatic response of the systems Cd(Hg)/OH$^-$, Tl(Hg)/Cl$^-$ and Hg/S$^-$, $\log(i/t^2)$ was found to be linear in $t^3$ implying progressive nucleation. From the slope of such straight lines the model parameter $\beta$ can be calculated. The concentration and potential dependence of $\beta$ help in fixing the elementary steps involved in the phase growth. Thus incorporation of
adsorbed Hg\(^+\) and adsorbed OH\(^-\), into the anodic lattice were identified as the rate determining steps in the formation of calomel and CdOH respectively.

1.6.6. Adsorption

Monolayer formation by means of random aggregation is termed as the adsorption (Figures 1.9 and 1.10).

Consider the process,

\[ \text{Me}^{z+}(\text{aq}) + ze^- \rightleftharpoons \text{Me (ad)} + \text{aq}. \]

Kinetics of this adsorption process is given by [Bosco and Rangarajan (1981 a)]

\[
\frac{de}{dt} = q_m - \frac{d\theta}{dt} \tag{1.36}
\]

where

\[
\frac{d\theta}{dt} = K_1^*(1-\theta)\exp(\alpha_zF\eta/RT) - K_2^*\theta\exp(-\alpha_aF\eta/RT) \tag{1.37}
\]

for Langmuir adsorption and

\[
\frac{d\theta}{dt} = K_1^*(1-\theta)\exp(\alpha_zF\eta/RT + \alpha'_c\theta) - K_2^*\theta\exp(-\alpha_aF\eta/RT - \alpha'_a\theta) \tag{1.38}
\]

for Frumkin adsorption.

Where \( \theta \) is the adatom density, \( K_1^* \) and \( K_2^* \) are the standard adsorption and desorption constants respectively and \( \alpha_c \) and \( \alpha_a \) are the cathodic and anodic charge transfer coefficients.
Figure 1.9. Typical Transients for Adsorption Nucleation Model with Instantaneous Nucleation. (a) Purely Monotonic Transient, (b) Nucleation-Growth, (c) Adsorption and Nucleation-Growth and (d) Interplay between Adsorption and Nucleation Growth Components.
Figure 1.10. Typical Transients for Adsorption Nucleation Model with Progressive Nucleation.
1.7. ELECTRODEPOSITION OF COMPOUND SEMICONDUCTORS

Electrodeposition of compound semiconductors for preparing economically viable terrestrial solar cells is the recent topic of interest. Electrodeposition has been conveniently used to produce large area electrodes inexpensively, utilising a technology readily adopted to industrial production. Many technologically important compound semiconductors have been prepared by this technique [Brenner (1964), Gorbunova and Polukaro (1967), Cuomo and Gambino (1968), DeMattei et al (1978), Fulop (1985), Keen and Farr (1962), Walsh and Herron (1991), Chandra and Khare (1987), Sahu (1990)]. Review on electrocrystallisation of semiconducting materials from molten salt and organic solutions are also available [Elwell (1972), Fulop (1985), Elwell (1981)]. Electrodeposition of binary and ternary cadmium chalcogenides from solutions containing both the metal and chalcogen has been a topic of recent experimental research. Ternary solid solutions attracted particular interest because of their advantages like tailoring suitable valency level, refractive index, non-linearity, band gap and lattice parameters with the choice of the composition parameter. Chalcopyrite compound semiconductors such as copper indium disulphide, copper indium diselenide, copper indium ditelluride and silver indium diselenide are
promising semiconductor materials due to their direct band gap, high absorption coefficient, low cost and abundance of constituent elements for preparing high efficient heterojunction devices. Both single crystal and polycrystalline samples of chalcopyrite materials are prepared from different methods [Feigelson (1990), Kazmerski and Wagner (1985), Shay and Wernick (1975), Pamplin (1979)]. Electrodeposited polycrystalline materials are preferred, where large area electrodes are needed.

Though electrocrystallisation is a powerful tool for the investigation of crystal growth mechanism [Budevski (1982), Durai et al (1986), Durai et al (1986 a), Durai et al (1987)] little progress has been made on the study of the kinetics and mechanism involved in the process of compound deposition. Recently, an elegant kinetic model has been reported [Engelken (1983), Engelken and VanDoren (1985), Engelken and VanDoren (1985 a), Engelken (1987), Engelken (1988)] for the ionic electrodeposition of cadmium telluride and other binary compounds from solution containing their respective reducible ionic species. The kinetic model is based on the diffusion controlled Butler-Volmer equation. The model has been developed utilising both the thermodynamical concepts concerned with the behaviour and magnitude of equilibrium potential and the kinetics explaining the individual process and their rates.
In the present investigation electrodeposition of binary chalcogenides and their ternary solid solutions, ternary chalcopyrite compounds was carried out from an aqueous solution containing their respective reducible ionic species by both potentiostatic and periodic pulse techniques. The deposited materials have been characterised with X-ray diffractograms, scanning electron microscopy, electron probe micro analysis, electron spectroscopy for chemical analysis and voltammetry.

Electrocrystallisation kinetics of binary compounds such as GaAs, CdS, CdSe etc., has been analysed by extending the model developed for CdTe. Further, the theoretical model corresponding to the electrodeposition of \( \text{AB}_x\text{C}_{1-x} \) and \( \text{ABC}_2 \) systems have been derived and presented for the first time in literature. The simulated results through the theoretical model are compared with the experimentally observed values. The details of the model developed to understand the electrodeposition process of these (AB, \( \text{AB}_x\text{C}_{1-x} \) and \( \text{ABC}_2 \)) compounds, the evaluation of optimum condition for codeposition and the results on characterisation of these electrodeposited compounds are presented in the following.