CHAPTER II
THEORETICAL BACKGROUND OF THE
EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

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CHAPTER – II

THEORETICAL BACKGROUND OF THE EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

2.1 INTRODUCTION

This chapter describes various theoretical aspects related to the preparation and characterization of MoSe$_2$, WSe$_2$ and Mo$_x$W$_{1-x}$Se$_2$ films. During the past few decades there has been a virtually a revolution in electroplating industry. Electrodeposition offers the hope of a means of conveniently producing large area samples inexpensively, utilizing a technology readily adaptable to large scale industrial production. It is widely employed for coating hardware to protect it from corrosion, making it decorative and hard, in the manufacture of metal copies and printed circuit boards in electronic industry. Particularly, electrodeposition is a method of preparation of thin film semiconductors useful for flat panel displays and for the fabrication of solar cells and various electronic devices.

Some of the main advantages of the electrodeposition technique are:

1) It is possible to grow uniform films over large areas, as well as over irregularly shaped surfaces.

2) Compositionally modulated structures or non-equilibrium alloyed can be electroplated.

3) It is specially attractive in terms of cost, high throughput and scalability.
The use of modulated current in electrolysis is by no means new. The first application of periodically interrupted current dates back to the end of the last century, when it was used by Coehn [1] to produce coherent deposits of zinc. Baeyens [2] reviewed applications of various types of modulated current upto 1952, and Dini [3] has reviewed the main work carried out upto 1963 with reverse current, i.e. current comprising an anodic component in the interval between cathodic pulses.

The electrical double layer at the electrode-solution interface can be approximated to a plate capacitor with an interplate distance of a few angstroms and therefore with a high capacitance. Charge must be provided to this double layer in order to raise its potential to the value required to metal deposition at the rate corresponding to the applied pulse current which is supplied by the generator. The charging of the double layer requires a certain time which depends on the current density and on other physicochemical parameters of the system. For practical purposes of charging time should be much shorter than the pulse duration, otherwise the current pulse is strongly distorted. Moreover, the time required for discharge of the double layer should be much shorter than the off - time between two pulses.

In the immediate vicinity of the cathode the concentration pulsates with the frequency of the pulsating current, decreasing during the pulses and relaxing in the interval between them. Thus a pulsating diffusion layer exists close to the cathode. If the duration of the pulse is short, the diffusion layer does not have
time to extend very far into the solution and in particular does not extend to the region where convection takes over the mass transport. Therefore the metal deposited during the pulse must be transported from the bulk of the solution towards the pulsating diffusion layer by diffusion, which means that a concentration gradient also builds up into the bulk of the electrolyte. The maximum pulse duration is called the “transition time”. The first limitation due to the mass transport effect in pulse plating is the pulse duration should not exceed the transition time, while the second is the maximum average current density can not exceed the Direct Current (DC) limiting current density.

The crystallization of the electrodeposited metal is a very important step of the electrogrowth since it influences directly the structure of the deposit. The crystallization is the process by which the adatoms or adions incorporate in the crystal lattice. Crystallization occurs either by the build-up of old crystals or the formation and growth of new ones as shown in Fig. 2.1. These two processes are in competition and can be influenced by different factors. High surface diffusion rates, low population of adatoms, and low over potentials are factors enhance the build-up of old crystals, while conversely low surface diffusion rates, high population of adatoms and high over potentials on the surface enhance the creation of new nuclei. In pulse plating, since the pulsed current density is usually higher than the corresponding DC density, the population of adatoms on the surface during pulse deposition is higher than during DC deposition. Another phenomenon that might occur in pulse plating during the off-period is recrystallization. To avoid this, the surface should remain active during the off-
Fig. 2.1. Crystallization mechanisms.
time. Again depending different adsorped species, the surface may be inhibit in which case no recrystallization will occur, and the fine grains obtained during the on-time of electrolysis are stabilized.

In pulse plating, the electrodeposition rate can be considerably increased during the on-time as compared to DC. Electrolysis can be controlled by regulation of either current or voltage. In current regulation mode, the reaction rate is kept constant and the potential varies as a function of time. In voltage regulation, the driving force for the reaction is kept constant and the reaction rate varies as a function of time. From a practical point of view, regulation of pulse voltage is very difficult to achieve. So for in most applications, however current regulation is preferred. The main advantages of pulse plating are:

- the improvement of deposit properties namely, porosity, ductility, hardness, electrical conductivity, wear resistance and roughness.
- deposition of alloys, the composition and structure of which are not obtainable with DC plating.
- improvement of plating thickness distribution by periodic inversion of polarity.
- increase in average deposition rate, although this can be achieved only to a rather limited extent.

2.2 Basic Concepts of Electrodeposition

Thin films can be prepared either by physical methods (e.g. thermal evaporation, sputtering, epitaxial growth) or by chemical methods (e.g.
anodization, chemical vapour deposition (CVD), chemical bath, electrodeposition). Physical methods are expensive but give relatively more reliable and more reproducible results. Most of the chemical methods are cost effective, but their full potential for obtaining device quality films has not been fully explored in many cases. Electrodeposition offers the following attractive features for the preparation of thin film solar cells [14].

- It is an isothermal process mainly controlled by deposition potential which can be easily adjusted.
- It is operated at low potential and at any suitable temperature. Thus, saving energy, it produces sharper junction without deleterious effects of inter diffusion, concentration and dopant redistribution.
- It is particularly suited to fabricate hetero junction solar cells.

A very attractive feature of electrodeposition is that the plating could be employed as one of the steps in preparing binary or ternary alloys as photoelectrode materials or superconductors [15-24]. This has led to the making of new alloys and metallic compounds now required for specialized jobs. An electrodeposition system consists of the following components.

(i) **Electrolyte**

The electrolyte or bath provides the ionic species of elements 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 the improvement of its adhesion, surface finish and uniformity.

(ii) Electrodes

At least two electrodes (anode and cathode) are necessary. An applied field across these provides the main "driving force" for the ions. The positive (M\(^{2+}\)) and negative (X\(^{2-}\)) ions deposit (some exemptions exist) at the cathode and anode, respectively. Cathodic deposition is more popular in electrodeposition because:

- most metal ions are positive ions, and
- anodic deposition has been found to give poor stoichiometry and adhesion.

(iii) Power Supply

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

Electrodeposition is a method by which any substance is deposited onto an electrode as a consequence of passage of electricity through it. The phenomenon of electrolysis is governed by the following Faraday's laws of electricity first formulated by Faraday in 1833.
• The mass of material undergoing electrochemical change is proportional to the quantity of electricity passed, and

• The masses of different species deposited at or dissolved from electrodes by the same quantity of electricity are in direct proportion to their chemical equivalent weights.

Mathematically the two laws may be combined and expressed as

\[ W = \frac{IZT}{F} \]  

(2.1)

where \( W \) is the substance (in gms) deposited, \( I \) is the current (in amperes) \( Z \) is the equivalent weights (in gms) \( T \) is the time (in seconds) and \( F \) is the Faraday constant equal to 96,500 coulomb (the amount of charge required to deposit one equivalent of any ion from the solution).

2.3 VARIOUS STEPS INVOLVED IN THE GROWTH OF AN ELECTRODEPOSIT

The entire pathway for the growth of an electrodeposit is illustrated in Fig.2.2(a). It can be divided into the following steps:

Step-1 Transport of ions in the electrolyte towards the interface.
Step-2 Discharge of ions reaching the electrode surface, giving rise to adatoms.
Step-3 Nucleation and growth. Two alternative routes are possible
   Route – A: Growth assisted by surface diffusion Fig.2.2(b)
   Route – B: Growth assisted by the formation Fig.2.3 of clusters and critical nuclei.
Step-4 Formation of monolayer and final growth of electrodeposit.
DIFFUSION TO A GROWTH SITE

STEP III (ROUTE A) (ROUTE B)

DIFFUSION TO A GROWTH SITE

STEP IV (MONOLAYER FORMATION)

FORMATION OF GROWTH CENTER

STEP IV (MONOLAYER FORMATION)

Fig. 2.2. Electrodeposit growth assisted by surface diffusion

(i) surface diffusion of adatoms
(ii) attachment of diffusing adatoms at kinks, and
(iii) continuous growth of electrodeposits at kink site
2.3. Various stages (a-d) of growth of an electrodeposited layer assisted by the formation of critical nuclei.
2.4 PARAMETERS INFLUENCING PULSE ELECTRODEPOSITION

2.4.1 Current Density

Current density is the total current divided by the electrode area. Within certain limits, as the current density is raised to the growth of nuclei enhances and the deposits will be fine grained. Further increase in current density gives foggy and spongy deposits. If the limiting current density exceeds, the concentration of metal in the cathode film decreases and the polarization increases. At low current densities discharge of ions occurs slowly, and thus the rate of growth of nuclei exceeds the rate at which new ones form. The deposit obtained under these conditions will be coarsely crystalline. Therefore, the limiting current density in a given solution should be used to control the composition, thickness and grain size of the deposit.

2.4.2 Bath Composition

The composition of the bath and pH plays an important role in the deposition process. The main constituent of the bath is the electrolyte, which serves as the source of ions. The ions may be in their simple form or of complex form. Depending on whether the process is cathodic or anodic, the nature of the anions or cations can strongly influence the structure of the film deposited, so that the ions are preferentially absorbed at the electrode – electrolyte interface forming a part of the inner row of the double layer.

For the same reason, certain organic molecules can afford a similar control. In some cases, suitable wetting agents may be used to promote the
detachment of the hydrogen bubbles from the cathode surface and thus prevent pitting caused by hydrogen evolution in the cathodic deposition process. If the electrolyte itself is not very conductive, acids, alkalies or suitable salts that are highly ionizable are used to achieve the required conductivity and to control the pH of the bath. The pH controls the conductivity of the electrolyte. However, a suitable value has to be determined because too low pH value may result only in hydrogen evolution, whereas too high value may cause the inclusion of hydroxides in the deposit. The temperature of the bath controls the rate of diffusion of the ions, the conversion current and decomposition of additives [25, 26].

2.4.3 Agitation

Agitation of the solution, in general, brings up a fresh supply of metal ions to the cathode, and thus helps in replenishment of metal ions at the cathode surface. Also agitation permits higher concentration densities to be used and increasing the limiting current density for obtaining thicker deposits.

2.4.4 Temperature

The rise in temperature enhances the rate of diffusion and increases the ionic mobilities consequent upon which the conductivity of the bath is increased. In general, an increase in the temperature of deposition causes an increase in the crystal size. This increase in crystal size corresponds to a decrease in polarization at the higher temperature. At higher temperatures, higher current densities are possible and hence it is possible to obtain fine-grained and smooth
deposits by intentionally heating the bath solution. At higher temperatures, cathode film is replenished rapidly and tendency towards treeing is reduced.

The opposing effects of temperature make it difficult to predict the best temperature of operation for any given bath, therefore, it is required to determine experimentally.

2.4.5 Electrode Shape

The distribution of current across the electrodes and hence the uniformity of the deposited films is affected by the shape of the active electrode. Higher current densities at edges and projections, compared to crevices and hollows, lead to thicker deposits on the edges. Hence the current density across the electrode must be kept constant and the surface of the electrode over which the film is to be deposited must be plane.

2.4.6 Duty Cycle

Duty cycle is defined as the ratio of (Pulse ON time) to (ON + OFF time) x 100%. By keeping the ON times were 1, 2, 3, 4 and 5 seconds with corresponding off time fixed as 1, 3, 7, 16 and 45 seconds the duty cycle was varied as 10, 20, 30, 40 and 50 percentages and the growth kinetics was carried out. For all the three cases MoSe2, WSe2 and Mo,W1,xSe2 the duty cycle was varied and the growth kinetics was studied. In the case of MoSe2 and Mo,W1,xSe2 the film thickness was reasonable and attain saturation after 60 min
for 30% duty cycle, and for WSe$_2$ 20% was found to be better. The detailed growth kinetics was discussed in chapter 2.8.

2.5 THEORY OF PULSE PLATING

Using pulse plating one can think of producing amorphous metals or alloys, for instance, from transition metals alloys to metalloids. In pulse plating with very high pulse current densities, the concentration of adatoms at the interface is so high during the pulse that there is no time for ordering them into a crystal lattice, resulting in similar effects, as in rapid quenching. The application of pulsed electrolysis to the electroplating of pure metals and alloys has attracted considerable attention since the early 1970s. There is a wealth of information on the mass transfer of pulsed electrolysis. Cheh [27,28] defined the concept of limiting current density and adopted a Nernst diffusion model to estimate the rate of mass transfer in pulsed and periodic reverse plating. Pulsed electrolysis affects the reaction kinetics in two ways. First the abrupt changes in the applied current density at both the beginning and at the end of a pulse cause a change in the state of the electrical double layer. The charging and discharging of the electrical double layer affect the faradic current which governs the rate of plating. Second, the change in the surface concentration of metal ion influences both the kinetics and the structural aspects of the plating system.

The electrical double layer at the electrode solution interface can be approximated to a plate capacitor with an interplate distance of a few angstroms and therefore with a high capacitance. Charge must be provided to this double
layer in order to raise its potential to the value required for metal deposition at the rate corresponding to the applied pulse current which is supplied by the generator. The charging of the double layer requires a certain time which depends on the current density and on other physicochemical parameters of the system. For practical purposes the charging time should be much shorter than the pulse duration, otherwise the current pulse is strongly distorted. Moreover, the time required for discharge of the double layer should be much shorter than the off – time between two pulses.

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voltage is very difficult to achieve. So far most applications, however current regulation is preferred.

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- deposition of alloys, the composition and structure of which are not obtainable with DC plating
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2.5.1 ELECTROLYTES

The influence of pulse plating on the deposition of bright zinc layers on steel substrates using commercial high cyanide (100 g / / NaCN) as well as low acid ammonium chloride - containing solutions was investigated by Paatsch [29]. Further work on low acid bright zinc electrolytes (60 g / / ZnCl₂, 300 g / / NH₄Cl, pH = 4 - 7) was done by Krivtsov et.al. [30,31] and Gadsov [32]. Some informations have appeared in the literature on the use of pulsed current for electroplating porous zinc layers for battery operations using concentrated alkaline zincate solutions (35 percent by weight KOH, 60g / / ZnO) [32,36].
2.5.2 Plating rate

Very little information has been given in the literature concerning the deposition current efficiency using pulse plating. In agreement with pulse plating theory [37] according to reference [31] the limiting overall plating rate of zinc generally does not exceed the values for DC plating conditions.

The pulse current density influences the concentration at the electrode, but not the deposition mechanism. This is possible however if two or more competing reactions take place in the deposition process e.g., the metal ion discharge and hydrogen evolution. As both reactions show different kinetics and current efficiency values, it can be possible to exceed the DC plating rate using suitable pulse plating parameters. Using a cyanide bright zinc electrolyte (131 g / / NaCN, 130 g / / NaOH, 52 g / / Zn) and an average current density of \( j_m = 1 \text{A} / \text{dm}^2 \), the metal deposition current density exceeds the value for DC conditions by about 10 percent with increasing pulse duration and duty factor. Choosing \( j_m = 8 \text{A} / \text{dm}^2 \), a maximum plating rate about 30 percent higher as compared to the DC value can be obtained for \( T_{on} = 0.2 \text{ms} \) and duty factor \( \nu = 0.7 \) [29]. This result is in general agreement with hydrogen permeation experiments.

2.5.3 Structure

The most interesting advantage obtained with pulsed current zinc deposition is the formation of a finer grain sized layer structure, resulting in a more homogenous surface appearance [29-31]. The deposits show a finer grain size and a leveled surface if a shorter pulse duration (e.g., \( T_{on} = 0.1 \text{ms} \)) and
longer break times (e.g., $T_{\text{off}} = 1 \text{ ms}$) are used. This effect is due to an enhancement of the nucleation rate by the high pulse current density and the resulting high over voltage [32]. Krivtsov et al. [30] are of the opinion that the zinc surface will be partly deactivated during the break time by the adsorption of impurities.

High leveling zinc coatings of 80 – 85 percent reflectivity can be deposited from a low acid electrolyte without brightening agents (60 g / / ZnCl$_2$, 300 g / / NH$_4$Cl, pH = 4.7, $T = 20 – 25^\circ\text{C}$) if a pulse current density $j_p = 300$ to 400 A / cm$^2$, a pulse duration $T_{\text{on}} = 0.2$ to 0.35 ms and a frequency of 50 to 100 Hz are used [31]. It should be mentioned that plating baths with no organic additives are easier to handle and less expensive. As the layer structure and the hardness are closely correlated the micro hardness of zinc deposits was found to be higher for pulse plating conditions [38].

2.5.4 Corrosion behaviour

Corrosion tests of pulse plated and DC plated zinc using commercial cyanide and low acid bright zinc electrolytes were performed in standardized artificial climates [29]. No significant difference in corrosion behaviour was found in these tests, as well as in outdoor field tests under industrial and marine conditions. Corrosion potential measurements in different solutions did not give different values. The composition and therefore electrochemical activity of zinc deposits investigated, were about the same regardless of deposition procedure. However, Krivtsov et al. [31] found an enhancement of the corrosion behaviour of
pulse plated – layers as compared to the DC conditions, by a factor of 1.8 to 2.0. This effect is believed to be due to the reduced porosity of the layers formed under optimum pulse plating conditions.

It is suggested that corrosion during the break time activates the surface and inhibits surface diffusion, resulting in an increased nucleation rate during the following pulse period. Further work on the influence of pulse plating on the properties of deposited cadmium using commercial low acid and cyanide solutions show no significant differences with respect to the corrosion behaviour and the wear resistance [31, 32].

2.5.5 Hydrogen embrittlement

Especially for low – alloyed – high strength steel with a tensile strength higher than 1200 N / mm$^2$ being used, for example, in the building and aircraft industries, the phenomenon of hydrogen – induced delayed cracking is well known. Electrochemical hydrogen permeation measurements clearly show that the time period for the first zinc nucleation is most important with respect to penetration of the codeposited hydrogen into the base metal causing embrittlement [39]. Once a very thin but continuous zinc layer is built up, a barrier is formed preventing the hydrogen atoms from further diffusion into the base metal. In comparison to the diffusion behaviour under DC plating conditions, optimum reduction of hydrogen diffusion is obtained by pulse plating [40] with short current pulses (e.g., $T_{on} = 0.1$ ms) and small duty factors (e.g., $\nu = 0.09$). The effect is due to smaller grain size, decreased porosity of the deposited thin
barrier layer as well as a change of electrode kinetics. Additional tensile test experiments with high-strength steel specimens prove that hydrogen can be avoided to some extent by pulsed electrodeposition of bright zinc [41].

2.5.6 Porous Zinc layers from alkaline solutions

Zinc electrodes in storage batteries (e.g., nickel-zinc batteries) are subjected to the problem of formation of dendritic deposits during the discharge and charging processes. With regard to cycle life and efficiency, good adherent deposits of high porosity are needed. Compact spongy and dendritic layer can be deposited, however, depending on the current density. Zinc sponge relatively high zinc concentration in the electrolyte, occurring during electrolysis of zincate solutions. This phenomenon can be caused by the incorporation of colloidal particles of zinc hydroxide or very fine zinc particles into the cathode deposit, resulting in dendrites at a later growth stage. The dendritic growth was found to be mass controlled.

Despic and Popou [37] showed that compact deposits could be achieved by pulse plating using the same current density at which dendrites are formed under DC plating conditions. In these experiments zinc was deposited from a 1.5 M zincate solution in 5 M KOH on copper wires. In pulse plating, potentiostatic symmetric square wave pulses of different frequencies upto 10^4 Hz were used. With increasing pulse frequency, dendrite formation was reduced and compact deposits resulted. According to pulse plating theory, the thickness of the pulsating part of the diffusion layer is a function of the pulse duration. If the
thickness is small compared to the surface roughness of the base metal, which is sufficiently short pulse duration, compact deposits are formed. Similar results were deposited by Romanou [36]. For practical purposes, the cathodic pulse duration and the break time were equally chosen to be 5 ms and the anodic pulse duration to be 10 ms. Even for prolonged times of electrolysis, the formation of 1.5 mm thick, adherent deposits of about 50 percent porosity was possible.

### 2.6 ELECTROCHEMISTRY OF THE DEPOSITION PROCESS

The electrodeposition of semiconductor compound like any other chemical process is governed by thermodynamic considerations. In the case of electrodeposition, the reactions are thermodynamically unfavourable, if the overall free energy change ($\Delta G$) for the reaction is positive and the electrical energy supplies the needed energy to drive the reaction. Consider the case of an ion $M^{+m}$ being reduced to $M$

$$M^{+m} + me^- = M \quad (2.2)$$

The change in free energy is given by

$$\Delta G = \Delta G^0 + RT \ln \left( \frac{a_M}{a_{M^{+m}}} \right) \quad (2.3)$$

where $R$ is the gas constant, $T$ is the absolute temperature and $a_M$ is the activity of species, i.e. activity is used instead of concentration in equation (2.3) to account for the interaction of ions in solution or for the difference in reactivity of an atom in a molecule versus that of an atom in the elemental state where the
activity would be 1. In the solution case, activity is related to the concentration by the activity coefficient

\[ a = [M^m] \] (2.4)

Barrow [42] has given a more complete discussion of activity and activity coefficients. Using concentrations, equation (2.4) can be written as

\[ \Delta G = \Delta G^0 + RT \ln (1/[M^m]) \] (2.5)

It can be shown that \( \Delta G = -nFE \) (2.6)

where \( n \) is the number of electrons involved in the reaction, \( F \) is Faraday’s constant and \( E \) is the redox potential. Equation (2.5) can be written as

\[ \Delta E = \Delta E^0 - \frac{RT}{nF} \ln (1/[M^m]) \] (2.7)

where \( E^0 \) is the standard electrode potential for reaction in equation (2.2) referred to the standard electrode with \([M^m] = 1 \text{ mole/litre}.\)

A single electrode reaction such as given in equation (2.2) cannot stand alone since there must be a compensating reaction involving an oxidation process. The overall reaction can be represented by

\[ bA^{a^+} + aB^{b^-} = bA + aB \] (2.8)

and the electrode reactions are given by

\[ A^{a^+} + ae^- = A \text{ (reduction at cathode)} \] (2.9)

\[ B^{b^-} = B + be^- \text{ (Oxidation at anode)} \] (2.10)
The cell potential is given by

\[ E = E_0^A + E_0^a - \frac{RT}{abF} \ln \left[ \frac{1}{(A^+)^b \times (B^-)^a} \right] \]  

(2.11)

The reactions described in equation (2.9) through (2.11) are typical of those involved in the deposition of an elemental semiconductor such as silicon or germanium. In the case of deposition of compound semiconductors like MoSe₂, WSe₂ etc., the situation is somewhat complicated. In this case, two materials must be deposited at the cathode, and one of the species, the non-metal (Se) is normally considered anion. This component of the semiconductor must be introduced into the solution in a form such that it can be reduced at the cathode. This is done usually by using a starting compound that incorporates the desired non-metal as part of oxygen containing ionic species (SeO₂).

In general terms, the reactions involved in this deposition could be

\[ M^{m^+} + me^- = M \]  

(2.12a)

\[ NO_y^{2-n} + (2Y - n)e^- = N + YO_2^- \]  

(2.12b)

\[ O^2^- = 0.5 O_2 + 2e^- \]  

(2.12c)

Yielding an overall reaction

\[ 2M^{m^+} + 2NO_y^{2-n} + (m-n) O^2^- = 2MN + (Y+(m-n)/2) O_2 \]  

(2.13)

The cell potential \( E \) is given by

\[ E = E_0^A - \frac{RT}{(2Y+m-n)} \ln \left[ \frac{1/(M^{m^+})^2 \times [NO_y^{2-n}]^2 \times [O^2^-]^{m-n}}{1} \right] \]  

(2.14)
where $E_0$ is the sum of the $E_0$'s for reactions (2.12) a,b and c. From a practical point of view, it is important to ensure that reactions (2.9) and (2.10) occur simultaneously. This will occur, if the potentials of the two reactions are equal. The two cell reactions are

$$2M^{*+m} + MO^{-2} \rightarrow 2M + 0.5 \text{ m O}_2 \quad (2.15a)$$

$$2NO_{y-n}^{-n} \rightarrow 2N + (Y-n/2)O^2 + nO^{-2} \quad (2.15b)$$

with cell potentials given by

$$E_M = E_0^M - \frac{RT}{2mF} \ln \frac{1}{(M^{*+m})^2 [O^{-2}]^m} \quad (2.16a)$$

$$E_N = E_0^N - \frac{RT}{2 (2Y-n)F} \ln \frac{[O^{-2}]^n}{[NO_{y-n}^{-n}]^2} \quad (2.16b)$$

Where $E_0^M$ and $E_0^N$ are the sum of the standard potentials for reactions (2.12a) and (2.12c) and (2.12b) and (2.12c) respectively. Since the desired condition for codeposition is $E_M = E_N$ equation (2.16a) and (2.16b) can be combined to yield an expression for determining the solution for codeposition.

$$E_0^M - E_0^N = \frac{RT}{2mF} \ln \frac{1}{(M^{*+m})^2 [O^{-2}]^m}$$

$$- \frac{RT}{2 (2Y-n)} \ln \frac{[O^{-2}]^n}{[NO_{y-n}^{-n}]^2} \quad (2.17)$$

Equation (2.13) is useful only if the $E_0$'s are known for the various species in the solvent system being used. The $E_0$'s are usually obtained by using two methods (i) Pourbaix diagram [43,44] or (ii) Cyclic Voltammetry.

Equation (2.13) can be written by using a more simple model using activity coefficient [45].
\[ E_m = E_m^\circ - \frac{RT}{mF} \ln(a_m) \] (2.18)

\[ E_n = E_n^\circ - \frac{RT}{nF} \ln(a_n) \] (2.19)

\[ E_i = E_i^\circ - \frac{RT}{IF} \ln(a_i) \] (2.20)

where \( a_m, a_n \) and \( a_i \) are the activities of the alloy components. \( E^\circ \)'s are the standard potentials of pure metals, and \( E \)'s are the standard potentials for respective alloy components.

The limiting values of \( a_m, a_n \) and \( a_i \) are given by

\[ a_m = \exp \left( \frac{\Delta G^\circ}{pRT} \right) \]

\[ a_n = \exp \left( \frac{\Delta G^\circ}{qRT} \right) \]

\[ a_m' = \exp \left( \frac{\Delta G^\circ}{rRT} \right) \] (2.21)

respectively where \( \Delta G^\circ \) indicates the change in free energy for equation that follows:

\[ \text{M}^{m^+} + m \text{e}^- = \text{M} \] (2.22)

\[ \text{M}^{n^+} + n \text{e}^- = \text{N} \] (2.23)

\[ p\text{M} + q\text{N} = p\text{M}_p q\text{N}_q \] (2.24)

Similarly if we consider a third element 'L' is considered

\[ \text{L}^{l^+} + 1 \text{e}^- = \text{L} \] (2.25)

Then for a ternary compound like Mo\(_2\)W\(_{1+x}\)Se\(_2\) can be written as

\[ \text{P}^{\text{M}^+} + q\text{L}^{+\text{N}} = p\text{M}_p (\text{N}+\text{L}) q \] (2.26)

The reversible potentials for the above equation can be obtained from equations
\[ \Delta E_M = E_M + \left( \frac{RT}{mF} \right) \ln (a_{M^{m+}}) \]  
\[ \Delta E_N = E_N + \left( \frac{RT}{nF} \right) \ln (a_{N^{n+}}) \]  
\[ \Delta E_L = E_L + \left( \frac{RT}{lF} \right) \ln (a_{L^{l+}}) \]

where \( a_{M^{m+}}, a_{N^{n+}}, a_{L^{l+}} \) are the activities of the respective ions in the solutions. Therefore, the apparent potentials deviation \( \Delta E_M, \Delta E_N \) and \( \Delta E_L \) from the respective standard potentials by alloy from atoms are written as

\[ \Delta E^M = -\Delta G/p^mF \] \[ \Delta E^N = -\Delta G/q^nF \] \[ \Delta E^{(M^{m+}L^{l-})} = \Delta G/p^{(m+n)F} \] \[ \Delta E^{(L^{l+}N^{n-})} = \Delta G/p^{(l+n)F} \]

respectively.

### 2.6.1 Electrodeposition by a periodic (or) pulse source

In order to improve the quality of the deposit non-dc signals are also used for electrodeposition. Varying either the current or the potential can do non-dc electrodeposition. Current variation can be made by using a periodic reverse current (PRC), a pulsating current (PC) or alternating current (ac). Fig.2.4. shows some of the above mentioned commonly used waveforms. The periodic reverse anodic and cathodic current densities are \( j_a \) and \( j_c \) which flows through a semiconductor for time \( t_a \) and \( t_b \) respectively. Hence the average PRC density is

\[ J_{PRC, av} = \frac{I}{t_a} = \frac{j_c t_c - j_a t_a}{j_c + t_a} \]
When we assume anodic and cathodic cycle durations are equal

\[ J_a = j_c = J_{PRC} \]  \hspace{1cm} (2.35)

\[ J_{PRC, av} = J_{PRC} \times \left( \frac{1 - t_a / t_c}{1 + t_a / t_c} \right) \]  \hspace{1cm} (2.36)

In the case of pulsed current waveform Fig.2.4.1. (b) with 'on' time \( t_{on} \) and 'off' \( t_{off} \) the average current is

\[ J_{av} = j_p \left( t_{on}/t_p \right) \]

where \( t_p \) is the period of the pulse.

Fig.2.4. Some commonly used periodic and pulse waveforms for electrodeposition (a) Periodic reverse current; (b) galvanostatic current pulse; (c) Periodic reverse current with off time; (d) sinusoidal current; (e) potentiostatic pulse some of the merits of non-d.c. electrodepositions are summarized:

1) In normal dc electrodeposition one can vary only one parameter either the current or the voltage. But in non-dc electrodeposition at least any three parameters among four can be varied. The four parameters are anodic, cathodic current densities \( j_a, j_c \) and the anodic, cathodic duration \( t_a, t_c \) of the deposition cycle. Similarly in the case of pulse deposition one can independently change the pulse height, the pulse on and off times \( t_{on} \) and \( t_{off} \) respectively.

2) Instantaneous and abnormal current densities can occur in non d.c electrodeposition. This abnormal change can cause a large negative shift in the over potential.
Fig. 2.4. Some commonly used periodic and pulse waveforms for electrodeposition
(a) periodic reverse current
(b) galvanostatic current pulse
(c) periodic reverse current with off time
(d) sinusoidal current
(e) potentiostatic pulse
time of the cathodic pulse deposition, adsorption, desorption and recrystallization of the deposit can take place. Similarly, during the anodic cycle of the periodic reverse current, electropolishing of the deposit occur. Hence the properties of the electrodeposits can be drastically altered by suitably choosing the pulse duty cycle or the anodic or cathodic portions of the waveform. The over potential also can alter the nucleation rate. Amplification of surface inhomogeneities seen in dc deposition can be decreased under diffusion control. Therefore the deposit becomes more and more smooth.

The choice of the optimum frequency range is limited by the effect of the capacitance of the electric double layer at high frequencies and the mass transfer effect at low frequencies. The double layer has high capacitance and certain part of the applied current is spent in charging this double layer. As this double layer charging continues more and more current is used to drive the charge transfer reaction (\(J_{CT}\)). We see this effect in Fig. 2.5. The time \(t_{DL}\) corresponds to the double-layer charging time. Hence total current \(j\) is sum of \(j_{DL}\) and \(J_{CT}\). In Fig. 2.5.(a) The double-layer charging time is very small compared to the 'on' time \(t_{on}\) of the pulse. The charge transfer current can be considered practically equal to pulse current \(j\) at all times when the charging time is comparable with the pulse 'on' time we can have \(t_{DL} < t_{on}\) or \(t_{DL} > t_{on}\). In the first case Fig. 2.5.(b) the charge transfer current attains the value \(j\) only after a certain time lapse. Anyhow in the
Fig. 2.5. Capacitative effect of the double layer when
(a) $t_{DL} < t_{on}$; (b) $t_{DL} < t_{on}$ (c) $t_{DL} > t_{on}$ (d) $t_{DL} >> t_{on}$
latter case Fig. 2.5.(c) the charge transfer current never reaches total current \( j \). In both cases, we note that the discharge time is much longer than the 'off' time. In Fig. 2.5.(d) it is seen that the discharge time is much longer than the 'off' time so the double layer is never completely discharged. The charge transfer current never drops to zero and fluctuates only slightly from the average current \( j_{av} \). In other words, dc conditions are being approached. In such a situation it is useless to carry out pulse deposition.

The mass transfer under non-steady state conditions has been studied by a number of workers [4-12]. Fick's second law can be used to solve this problem. Non-steady-state diffusion to the cathode is given by

\[
\frac{\partial C^i}{\partial t} = \frac{\partial^2 C^i}{\partial x^2} \tag{2.37}
\]

Under boundary conditions, assuming linear diffusion

\[
C_i - C^0, \quad \text{at } x \geq 0; \ t=0 \tag{2.38}
\]

\[
C_i - C^0, \quad \text{at } x = x_c; \ t > 0 \tag{2.39}
\]

\[
\frac{\partial C^i}{\partial x} = \frac{j}{ZFD} \quad \text{at } x = 0; \ t > 0 \tag{2.40}
\]

Fig. 2.5. Capacitative effect of the double layer causing the damping of charge transfer current when (a) \( t_{DL} \ll t_{on} \); (b) \( t_{DL} < t_{on} \) (c) \( t_{DL} > t_{on} \) and (d) \( t_{DL} \gg t_{on} \)

Assuming that a stagnant layer of thickness exists at the cathode and using the additional boundary condition

\[
C_i - C^0, \quad \text{at } x \geq \delta; \ t > 0 \tag{2.41}
\]
Using the boundary conditions (2.38) - (2.40) and (2.41) and Fourier transformation, the diffusion equation can be solved to give [1]

\[ C_{i,x=0} = C^0_i - q (j \delta / zFD) \]  

(2.42)

with \( q = 1 - \left( \frac{8}{\pi^2} \right) \sum_{p=1}^{\infty} \frac{1}{(2p-1)^2} \exp\{-\left(\frac{(2p-1)^2}{4(Dt/\delta^2)}\right)\} \) \hspace{2cm} (2.43)

where \( p \) is an integer

For the special case when \( Dt/\delta^2 < 0.1 \) i.e., for large values of \( \delta \) and small values of \( t \) Eq.(2.43) can be approximated [2].

\[ q \approx 2/\pi^{1/2} (Dt/\delta^2)^{1/2} \] 

(2.44)

For small values of \( \delta \) and large values of \( t \) i.e., \( Dt/\delta > 0.1 \),

\[ q = 1 - \left( \frac{8}{\pi^2} \right) \exp\{-\left(\pi^2Dt/4\delta^2\right)\} \] 

(2.45)

For a convective system the transition time is reached only if the current \( j \) exceeds the steady-state limiting current \( j_1 \) given by

\[ J_1 = zFD C^0_i / \delta \]

For repetitive pulses, the boundary condition (2.40) can be replaced by

\[ \frac{\partial C_i}{\partial x} \big|_{x=0} = j_o / ZFD \quad \text{at} \quad x = 0; \quad ut_{on} > t(u-1)T = 0 \]

at \( x = 0 \quad uT > ut_{on} \)

where \( u \) is the number of pulses and \( T \) its period.
Ibl proposed a duplex diffusion layers using an extension of the Nernst approximation of a linear concentration profile in a dc diffusion layer. Ibl's model is schematically shown in Fig. 2.6

According to this model, a pulsating diffusion layer of thickness $\delta_p$ exists close to the electrode surface. The concentration in this layer decreases during the 'on' time and relaxes during the 'off' time.

For short pulse duration, the diffusion layer is not able to extend very far into the electrolyte regions where convection takes over the mass transport. A concentration gradient also builds up into the electrolyte, giving rise to an outer stationary diffusion layer $\delta_s$. This layer supplies ions to the pulsating diffusion layer during the 'off' time. The concentration of cations in the outer diffusing layer was assumed to be time-invariant. The pulse current $j_p$ is given by

$$j_p = zFD C^1_x \cdot C_{1,x=0} \over \delta_p$$  \hspace{1cm} (2.46)

where $C^1_x$ is the concentration at the outer boundary of the pulsating diffusion layer. The average current density is given by

$$j_{av} = zFD (C^0_x - C^1_x / \delta_s) = j_p \left(t_{on} / T_p\right)$$ \hspace{1cm} (2.47)

Equations (2.46) and (2.47) indicate that the concentration gradient in the pulsating layer is proportional to the pulsed current density while the concentration gradient in the outer stationary layer is proportional to the average current density. For very short pulses the concentration gradient in the former case can be made very large, and thus one can obtain very high instantaneous
Fig 2.6. Ibl's model of a duplex diffusion layer with a linear concentration profile.
current densities in pulse electrolysis. The thickness of the pulsating diffusion layer $\delta_p$ was obtained by considering the mass balance over the pulsating diffusion layer:

$$\delta_p = 2D_{ton} \left[ 1 - \left( \frac{t_{on}}{T_p} \right) \right]^{1/2}$$  \hspace{1cm} (2.48)

The pulsating diffusion layer thickness depends on the pulse duration and decrease with increasing pulse frequency.

At the outer stationary layer, the mass balance yields

$$C^* = C^*_{\infty} - \left( \frac{j_p}{zFD} \right) \left( \frac{t_{on}}{T_p} \right) \left\{ \delta - \left[ 2D_{ton} \left[ 1 - \left( \frac{t_{on}}{T_p} \right) \right]^{1/2} \right] \right\}$$  \hspace{1cm} (2.49)

where $\delta = \delta_p + \delta_s$

In the case of dc electrolysis, deposition under diffusion-limited conditions leads to the formation of powdery deposits due to the amplification of surface roughness. In pulse deposition the powder formation can be prevented as long as the pulsating diffusion layer is very thin compared to the micro profile of the electrode surface.

If limiting current pulses are used, the average current density $j_{av}$ becomes

$$j_{av} = j_p \left\{ \frac{\delta_p}{\delta} \left[ (T/\Delta t_{on}) - 1 \right] + 1 \right\}^{-1}$$  \hspace{1cm} (2.50)

Using this equation the average limiting rate of deposition can be calculated. The use of pulsed electrolysis is limited, by the mass transport effects in the electrolyte. Increasing the pulse current density $j_p$ results in increasing the depletion of the pulsating diffusion layer concentration, leading to $c_x = 0$. If the
pulse duration is longer than the transition time $i$ (the time within which $c_x = 0$ drops to zero), the electrodeposition can continue even for time $> i$, but the current efficiency will decrease the time interval $i$ to $t_{on}$. Since the boundary $c_x = 0$ is fixed, this will increase the outer depletion stationary layer. If the depletion becomes sufficiently strong, the electrodeposit may become powdery or dendritic due to increasing amplification of surface roughness. The advantage of pulse deposition will be lost. Therefore the pulse on time should not be longer than the transition time $T$ given by $I_{bl}$.

Current efficiency in pulse electrolysis is defined as the ratio of the charge transfer current to the pulse density averaged over the ‘on’ time $t_{on}$.

It was shown that the extent of localization in the cathode current distribution can be increased by (1) decreasing the pulse duty cycle (2) increasing the average anode current density and (3) increasing the anode - cathode spacing.

Popou et al have given the current during the on time for sufficiently high cathodic pulse of height $i_{dp}$:

$$j_{on} = j_{o} \left(1 - \left(\frac{j_{av}}{j_{o}}\right)\right) \exp\left(\frac{\eta_{dp}}{\eta_{o}}\right)$$

where $\eta_{o}$ is the slope of the Tafel plot. The current flowing during the off time is

$$j_{off} = j_{o} = \frac{j_{av}}{j_{o}}$$

and the average current density is given by

$$j_{av} = \frac{(j_{on} t_{on} - j_{off} t_{off})}{T}$$
Theoretical models for the pulse deposition of elemental semiconductors are expected to be similar to those for metals. But application to compound semiconductor electrodeposition is more complicated.[13]

2.7 GROWTH KINETICS

Thin films of MoSe$_2$, WSe$_2$ and Mo$_x$W$_{1-x}$Se$_2$ are pulse plated on transparent conducting oxide (TCO) coated glass substrates and on titanium substrates under galvanostatic mode using PC based pulse console potentiostat / galvanostat developed indigenously at CECRI, India. The TCO or titanium substrates were used as the cathode in the three-electrode cell with platinum as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The necessary electrolyte solution was prepared. The chemicals used were all G.R grade E-Merck. Before deposition, the substrates were thoroughly cleaned with triple distilled water and acetone to degrease the surface of TCO. The distance between the working electrode and the graphite counter electrode was kept 1 cm apart. The important deposition parameters are concentration, composition of the electrolyte bath, pH, bath temperature, time of deposition, deposition current / voltage and duty cycle. The graph drawn by taking time of deposition in minutes along the X-axis and the thickness of the deposited film in $\mu$m along the Y-axis, keeping anyone of the other deposition parameter as constant is known as the growth kinetics graph. From these graphs one can get idea about the optimized deposition parameter values. Then the deposition becomes much easier.
2.8 THEORETICAL ASPECTS OF VARIOUS CHARACTERIZATION TECHNIQUES

2.8.1 Structural studies

Structural characterization of single crystals and polycrystalline thin films coated over a substrate are usually done using X-ray diffraction (XRD) by the crystal planes obeying Bragg’s law of diffraction, which makes use of the principle of rotation of plane mirror Fig.2.7.

\[ 2d \sin \theta = n \lambda \]  \hspace{1cm} (2.51)

where ‘d’ is the interplanar distance, ‘\( \lambda \)’ is the wavelength of the incident X-ray beam ‘n’ order of reflection and ‘\( \theta \)’ is the Bragg angle. The diffraction pattern of the film or crystal indicates characteristics peaks at different Bragg angles from which interplanar spacing of the crystal or film may be determined using the relation (2.51). These peaks are identified using ASTM data to study the crystalline nature and structure of the films.

The lattice parameters ‘a’ and ‘c’ for the hexagonal structure are calculated using the formula

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{(h^2 + hk + k^2)}{a^2} \right) + \left( \frac{l^2}{c^2} \right) \hspace{1cm} (2.52)
\]

where \( h, k, l \) represent Miller indices and ‘d’ is the interplanar distance.

The grain size (L) of the films are estimated from the Debye-Scherrer formula
Fig. 2.7. Schematic diagram of X-ray diffractometer measured from the incident beam, the reflecting plane must be rotated $\theta$ and the detector to $2\theta$ for maximum intensity.
where $\lambda = 0.1542$ nm, $\beta$ is the full width at half maximum (FWHM) of the peak and $\theta$ is the Bragg angle.

The preferred orientation of the crystallites in thin films and the degree of crystallite order are determined by the method proposed by Janda and Kubovy [46]. The schematic representation of an X-ray spectrograph is shown in Fig.2.8.

2.8.2 Surface Morphological Characterization

(i) Scanning electron microscopy (SEM) Studies

To study the morphology of semiconductor film, simple reflection modes of the optical microscope can be extended. But these techniques are limited in spatial resolution to a few tenths of a micrometer. The extension of the resolution is allowed in electron beam techniques. The most versatile among these is Scanning Electron Microscopy (SEM). It facilitates obtaining highly magnified pictures of solid, conducting and non-conducting dry surfaces. The convenience of the conventional SEM is partly due to the long working distance between the final lens and the simple surface and partly due to the ability to directly study almost any free surface. Further, SEM offers several modes of operation. The most widely employed is secondary electron imaging, which gives images of better resolution, almost unlimited depth of field and good contrast [47,48].

The SEM photographs provide information on the nature of the surface. Film uniformity, smoothness, presence of cracks, the nature and size of grains can be known [48].
Fig. 2.8. Schematic representation of an X-ray spectrograph
(ii) Atomic force microscopy (AFM) Studies

AFM is a unique modern tool available for a real space view of the atomic structure and surface morphology of materials [48]. It is a surface structural technology, which is truly local in that it images individual atoms and does not rely upon long-range order to produce a signal. The technique is based on electron tunneling between a sharp metal tip and the surface of a conducting / semiconducting solid surface (as close as 5 to 10 Å), the wave function of the tip and the sample overlap and electrons tunnel between the tip and the surface of the solid.

If sufficient voltage is applied to the solid sample, there will be a net flow of electrons across the gap, which varies exponentially with the separation between the tip and the sample. The flow of electrons gives the tunneling current. The direction of electron flow depends on the sign of the bias voltage applied.

A map of the film / solid surface is generated by scanning the tip over the surface form side to side in parallel lines, keeping a constant tunneling current. Features in the map correspond to vertical displacements of the tip as it follows a contour of constant density of states at the surface of the sample.

The Nanoscope E Scanning Probe Microscopy systems Model No.3138 J has been used for the surface analysis of Mo_xW_{1-x}Se_2 films. Fig. 2.9 shows the experimental set-up for the AFM measurements. In the AFM measurements, a Topometrix Explorer system is operated in air in contact mode, with a typical scanning frequency of 0.5 – 1.0 Hz. In order to make electrical measurements,
Fig. 2.9. The block diagram of the AFM set-up
commercial Si tips are coated with a conductive layer of boron doped diamond. These wear-resistant conductive AFM tips have a radius of about 100 nm and a spring constant of 4 N/m. In order to establish a good electrical contact between the tip and the sample, a load of about 50 nN has to be applied. Under these conditions, the contact resistance between the tip and an evaporated gold film is typically 50 kΩ. Though a load of 50 nN is relatively high, no damage appears on the films, even after intense scanning. The current is measured with an external high-band pass (>10^4 Hz) Keithley K 429 current amplifier. The noise level for the current measurement is below 10 pA. The AFM electronics enable simultaneous acquisition of topography information and tip-sample current, as well as current voltage measurements at specific locations on the surface.

2.8.3 Optical Properties

(i) Absorption of light in semiconductors

Light interacts with a semiconductor by exciting electron transitions and atomic vibrations. The following four specific microscopic interactions between a light wave and a semiconductor are in various parts of the spectrum:

(i) Electron transitions from the upper part of the valence band to the lower part of the conduction band are responsible for the shape of the absorption spectrum and for the dispersion near the fundamental absorption edge. Electron transitions can be direct, without phonon participation and without change in the crystal momentum of an electron, or they can be indirect, in which the interaction with the
phonon produces a considerable change in the crystal momentum, if
the wavelength of that phonon is short (indirect transitions involving
long wavelength optical phonons take place like direct transition i.e.,
almost without any change in the crystal momentum of the electron).
The various types of transition give rise to different frequency
dependencies of the absorption coefficients near the fundamental
absorption edge. For the direct transitions, we have \( \alpha \propto (h \nu - E_g)^n \)
where \( E_g \) is the energy gap and \( n = 1/2 \), if the transition between the
extreme of the conduction and valence bands are allowed by the
selection rules and \( n = 3/2 \) if such transitions are forbidden. For the
indirect transitions, we have

\( \alpha \propto (h \nu - E_g)^n \) or \( E_g = E_g \pm E_{ph} \)

where \( E_{ph} \) is the photon energy, \( n = 2 \) for allowed transitions and \( n = 3 \)
for forbidden transitions. In the fundamental absorption range, light
generates electron - hole pairs and this gives rise to several
photoelectric effects.

(ii) Electron transition from deep states in the valence band to high states
upon the conduction band govern the optical properties in the short
wavelength (ultraviolet) part of the spectrum. If the energy acquired by
an electron is sufficiently high to overcome the surface barrier (work
function, photoelectric effect is observed).

(iii) The interaction of light with free carriers involves two types of electron
transitions, within one band and between bands of same type, for
example, between valence bands, one of which (the upper) contains holes. Transitions within one band cannot be direct because the absorption associated with such transitions is possible due to scattering.

(iv) The interaction of light with the lattice vibrations governs the absorption and dispersion in the far infrared region. Electromagnetic radiations interacts effectively with the transverse optical phonons and the natural frequency of the transitions is equal to the energy of these phonons. Fig. 2.10 illustrates the two types of optical transitions.

(ii) Determination of Optical Constants

Determination of ‘n’ and ‘k’ from the $R,T,R^0$ equations is an inverse problem. There is no analytical solution for the inverse problem of this kind and these unknowns can be obtained only through approximate formula or graphical or computational methods [49,50]. It is known that the set of non-linear algebraic or transcendental equations can be solved by the descent method [51]. The theory of continuous differential descent method [52] employed in this work is given below.

(iii) Continuous Differential Descent Method (CDD method)

The basis of the method for set of equations of the form

$$f_1 (X_1, \ldots, X_n) = 0$$

$$f_2 (X_1, \ldots, X_n) = 0$$
Fig. 2.10. "Direct interband optical transitions" for
(a) direct band and
(b) indirect band semiconductors the transitions are represented by vertical arrows.
If \( F(X) = 0 \) is the set of equations to be solved then the solutions sought through minimum points of the function \( u(x) = |F(X)|^2 \) by means of the set of equations

\[
dx_i / dt_i = -\sum_{j=1}^{n} f_j \left[ \left( \sum_{k=1}^{n} f_k \left( \frac{\partial f_j}{\partial x_k} \right) \right) / \left( \sum_{k=1}^{n} \sum_{i=1}^{n} f_k \left( \frac{\partial f_i}{\partial x_k} \right) \right) \right] \tag{2.55}
\]

For almost all initial points, the differential descent trajectory \( dx/dt \) approaches the minimum point of the function \( u(x) \). It has been proved that this point is the solution of the set of transcendental equations. The solution can be obtained by using numerical iteration methods. The Continuous Differential Descent equations from T and R have the form

\[
\frac{dn}{dt} = -(f_n^2 + f_i^2) \left( \frac{\partial f_n}{\partial n} \right)^2 + \left( f_n \frac{\partial f_i}{\partial n} \right)^2 + \left( f_n \frac{\partial f_i}{\partial k} \right)^2 \tag{2.56}
\]

\[
\frac{dk}{dt} = -(f_k^2 + f_i^2) \left( \frac{\partial f_k}{\partial n} \right)^2 + \left( f_k \frac{\partial f_i}{\partial n} \right)^2 + \left( f_k \frac{\partial f_i}{\partial k} \right)^2 \tag{2.57}
\]

where \( dn/dt \) and \( dk/dt \) are the trajectories of the continuous descent to the minimum points of the function,

\[
u = |F(n, k, t)|^2 \text{ and}\]

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\[ f_T = T - F_T(n, k, t/\lambda) \]

\[ f_R = R - F_R(n, k, t/\lambda) \]  \hspace{1cm} (2.58)

Any other pairs of equations \((T, T')\) and \((R, R')\) as initial pairs of measurement gives the same results. The CDD algorithm is developed using the equations as shown in Fig.2.11. This algorithm is used in a computer routine to get the value of \(n\) and \(k\).

The CDD method [17] has been used for the determination of optical constants for sprayed and electrodeposited thin films [53].

**2.8.4 Conductivity Type by Hot Probe Method**

The type of majority carriers determines if a semiconductor belongs to the \(n\) or \(p\)-type. In the former electrons, and in the latter holes are the majority carriers. It is possible to determine the type of conductivity by thermo electric power measurement [54]. The hot-probe technique is based on this principle.

The partial film coating on \(\text{SnO}_2\) conducting glass substrates are used. The cold junction is the conducting substrate which is connected to the hot tip of a soldering iron. When the hot probe momentarily touches the semiconductor layer, current flows from the cold junction to the hot junction for \(n\)-type and the reverse is for \(p\)-type semiconductors. All \(\text{Mo}_x\text{W}_{1-x}\text{Se}_2\) films show \(p\)-type nature.
DATA
\[ \lambda, d, n_1, n_2, T, R, n_0, k_0 \]

\[ i = 1 \]

\[ t = 1 \]

SOLVE CDD SET USING RUNGE-KUTTA METHOD
FIND \( n_i, k_i \)

CALCULATE
\[ |T - T_{cal}(n_i \cdot k_t)| \]
\[ |R - R_{cal}(n_i \cdot k_t)| \]

IF
\[ \varepsilon = 10^{-4} \]
IS
\[ |T - T_{cal}(n_i \cdot k_t)| \leq \varepsilon \]

RESULTS
WRITE
\[ \lambda_i, n_i, k_i \]

\[ \lambda_i = \lambda_{final}? \]

YES

STOP

NO

NEXT CYCLE
\[ i = i + 1 \]
\[ \lambda = \lambda_i \]
\[ n_0 = n_i \]
\[ k_0 = k_i \]
\[ T = T_i \]
\[ R = R_i \]

Fig. 2.11 Flow chart for CDD method
2.8.5 Measurement of Resistivity

The measurement of resistivity is not straightforward for electrodeposited semiconductors because the electrodeposits are necessarily on a metallic (conducting) substrate. Therefore, reports on resistivity measurements of electrodeposits are scanty [55]. The following two situations may arise:

1. The metal substance forms a low resistance ohmic junction with the semiconductor electrodeposit. In such a case, a two electrode sandwich arrangement with M/S/M symmetric geometry gives reasonable results. To test this, the current-voltage characteristics in both forward and reverse bias are plotted and symmetric plot should result. From the slope of the current-voltage plots, the resistivity $\rho$ can be calculated as

$$\rho = \frac{\rho V}{\rho I} \times A/t \quad (2.59)$$

where $A$ is the area of cross section of the deposit,

$t$ is the thickness of the thin film.

2. The metal forms a non-ohmic contact (i.e., the I-V curve is non symmetric) or the contact resistance is high. In this case the two-electrode method fails. This is the most common situation. The possible solutions are:

(a) All or part of the film is lifted by using an "adhesive tape" technique. The resistivity measurements were done using the Two-Point Probe and the Four Probe (Van der Pauw) techniques. This has a serious limitation if the electrodeposit has good adhesion, because in that case high force
will have to be applied to lift the film, which may cause damage to the thin film deposit.

(b) If the substrate sheet resistivity is of magnitude higher than the resistivity of semiconductor deposit then one can approximate the substrate as insulating and follow the Van der Pauw technique. The limitations of this method are quite obvious because it is hardly possible to get good large area electrodeposits on substrates with high resistivity.

The effect of contact resistance can be eliminated by use of the two-point probe technique shown in Fig 2.12. if the specimen cross section is uniform.

Measurements are done with very low current enough to prevent heating of the sample, the voltmeter must have high input impedance, and measurements must be made enough away from the contacts that any minority carriers injected might have already recombined. To minimize the equipotential lines that arise due to poor contact, the maximum cross-sectional dimension be not more than one-third the length of the sample and take measurement at the midpoint of the bar. If more than one set of measurements is to be made on a given sample, reproducibility will be improved.

Automatic two-point-probe instruments have been developed. Some even measure the crystal diameter at point of resistivity measurement, and provide automatic data print out of the position measurement, crystal diameter at that point, and resistivity[13]. Advantages of such systems are speed of evaluation and a minimization of human errors.
Fig. 2.12 Two point resistivity geometry. The voltage probes have fixed spacing and are moved in unison along the surface.
Most Czochralski-grown silicon crystals have a radial-resistivity variation as well as a longitudinal one. Because of the radial component, the resistivity measured by both the method are not one and the same.

\[
\frac{V}{l} = \frac{S}{2\pi} \int_0^{R_o} r dr \rho(r)
\]  

(2.60)

Where \( R_o \) is the radius of the ingot. By taking both readings and assuming the functional form of radial gradient, its magnitude can be estimated [56].

A single movable probe can be used and the voltage measured between it and a current lead or other suitable reference. By making several observations, \( dv/dx \) can be calculated and the resistivity can be calculated using the relation

\[
\rho = \frac{1}{x} \frac{dV}{da}
\]

(2.61)

where \( S \) is the probe spacing in centimeter,

\( x \) is the distance along the surface, \( s \) is the probe spacing in centimeter,

\( \rho \) is the resistivity[57].

2.8.6 Composition Analysis using X-ray Energy-Dispersive Analysis (EDAX)

Most energy-dispersive X-ray analysis systems are interfaced to SEMs, where the electron beam serves to excite characteristic X-rays from the area of the specimen being probed. To the SEM column a liquid-nitrogen Dewar flask is
attached, the cooled Si (Li) detector aimed to efficiently intercept emitted X-rays. The Si (Li) detector is a reverse-biased Si diode doped with Li to create a wide depletion region. The incoming X-ray generates a photo electron that automatically dissipates its energy $h\nu$ to create hole-electron pairs. The incident photon energy is linearly proportional to the number of hole-electron pairs produced i.e., the amplitude of the voltage pulse they generate when separated.

The pulses are amplified and then sorted according to the voltage amplitude by a multi channel analyzer, which also counts and stores the number when given increments of the voltage (energy) range. The result is the characteristic voltage shown for the constituent elements which occurs in multicomponent samples or when neighbouring elements in the periodic table are present. The schematic representation is indicated in Fig. 2.13.

Characteristic X-rays can also be generated using incident photons and energetic particles rather than electron as the excitation source. For example, conventional X-ray tubes, and radioactive sources such as [58] Am (60 KeV gamma ray, 26.4 KeV X-ray and Cd (22.1 KeV Ag-K X - ray) can excite fluorescent X-rays from both thin film and thick specimens. Unlike electron-beam sources, they have virtually no lateral spatial resolution. Fig.2.14 indicates the EDAX spectrum of a sample containing 3 rare earth elements Y(yffriwee) Sm (Smarium) and GD (Goldlinium). EDAX picture is a graph drawn by taking energy of the incident X-ray photon in KeV along the X-axis and the corresponding intensity coming out form the multichannel analyzer taken along the Y axis. From
Fig. 2.13. Electron excitation processes in T,  
(a) energy level scheme;  
(b) EDX spectrum of T, employing S, (L,) detector
Inclusion

Fig 2.14. Energy dispersive X-ray spectra indicating that the inclusion of rare earth elements, probably as complex oxides.
this one can get information about the constituent elements in a compound over which it is being deposited and also the atomic weight percentages of the constituent elements from which one can confirm whether the film is stoichiometric or non-stoichiometric in nature.

2.9. CONCLUSION

The various aspects related to the structure, optical and electrical studies have been described. The theoretical background necessary for the understanding of electrodeposition and pulse plating process are discussed. The growth kinetics for the film deposition are briefly described. The determination of optical constants using an iterative technique is also given in this chapter. The electrical resistivity measurements can be made using two-point-probe technique assuming the film thickness as a uniform one. EDAX study can be made to find the atomic weight percentages of the constituent elements present in the semiconducting compounds MoSe₂, WSe₂ and MoₓW₁₋ₓSe₂ (x = 0.25, 0.50 and 0.75).
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