
Study of Factors Influencing Electrodeposition of Thin Film.

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Abstract

There are various techniques to deposit solid semiconducting materials in the form of thin layer called as thin film. Electro deposition is one of these techniques. It is the process of depositing substance by passage of electric current through the conducting medium called electrolyte, producing a chemical change. The property of electrodeposited film depends on electrolyte, pH of the electrolyte, electrode nature, Potential and current density. The article discusses effect of these parameters on formation mechanism of thin films along with basic study of the method.

1. Introduction

A wide variety of processing technologies are available for the deposition of thin films. The technologies differ to a large degree in their physical and chemical principles of operation and in commercially available types of equipment. Each processing technology has been developed because it has unique advantage over others. However, each processing technology has its limitations. In order to optimize the desired film characteristics, a good understanding of the process control and the advantages and restrictions applicable to each technology is necessary.

Electrodeposition, which is one of these deposition techniques, is as old as the electricity. Electrodeposition of metallic films

(commonly known as electroplating) has been known and used for preparing metallic mirrors and corrosion-resistant surfaces. It is also used in electroforming, i.e., to give shapes to electrodeposits. In recent years, there has been considerable interest in the electrodeposition of semiconductor films for photovoltaic applications. In this article an attempt is made to focus electrodeposition technique for deposition of thin films due to following advantageous factors.

- Synthesis is possible at low temperatures with less instruments
- Doping of is possible during synthesis.
- Liquid materials can be easily converted into thin films with required quantity, different size and shapes.

2. Electrodeposition

Electrodeposition of metals and alloys involves the reduction of metal ions from aqueous, organic, and fused-salt electrolytes by the passage of an electric current. It is based on the study of reactions in which charged particles cross the interface between two phases of matter, typically a metallic phase (the electrode) and a conductive solution, or electrolyte. A process of this kind is known as an electrode process. The first quantitative formulation of electrodeposition was done by Michael Faraday, popularly known as Faraday's laws of electrodeposition.

2.1 Basics of Electrodeposition

i. Faradays First law

The total amount of chemical change produced by an electric current is proportional to the total charge passing through the electrolyte.

ii. Faradays Second law

When same quantity of electricity is passed through different electrolytes arranged in series, the weights of substances liberated at the respective electrodes are directly proportional to their chemical equivalent weight.

$$W = (E/F) ct$$

Where E is equivalent weight and c , t are current and time respectively with $F = 96485$ C/mol. However in practice the problem is much complicated and factors like sticking of electrodeposited atoms, Joule heating affect the efficiency of the process.

iii. Nernst Equation

When a solid is immersed in a polar solvent or an electrolyte solution, surface charge will develop and the electrode attains a potential given by the Nernst equation [3]

$$E = E_0 + (RT/nF) \cdot \log_e (a_{ion})$$

where E_0 is the potential difference between the electrode and the solution when the activity a_{ion} of the ions is unity, F is Faraday's constant, R is the gas constant, and T is the temperature. [3]

2.2 Components of Electrodeposition Technique

i. Electrode

At least two electrodes (cathode and anode) are needed for deposition process Fig.[1]. An applied electric field across these electrodes provides the main driving force for the ions. The positive M^+ and negative x^- ions deposit at cathode and anode respectively.

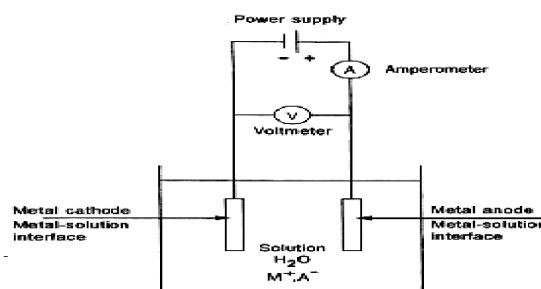
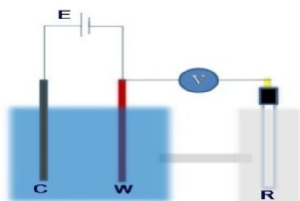


FIG.1: Two Electrode Cell

1) Cathodic deposition is more popular in electroplating because most metal ions are positive ions. 2) Anodic deposition gives poor stoichiometry and adhesion.

In most electrochemical experiments our interest is concentrated on only one of the electrode reactions. Since all measurements must be on a complete cell involving two electrode systems, it is common practice to employ a reference electrode as the other half of the cell.

Fig.2



C- Counter Electrode
R- Reference Electrode
W- Working Electrode

FIG.2: Three Electrode Cell

The major requirement of a reference electrode is that, its potential must be stable. It is achieved by involving a saturated solution of an insoluble salt of the ion. The common reference electrode is the calomel electrode.[3]

ii. Electrolyte

The electrolyte or bath provides the ions to be electrodeposited. It has to be electrically conductive. It can be aqueous, non-aqueous or molten and it must contain suitable metal salts sometimes additive is included to improve the quality of electro deposit and to achieve uniform surface finish.

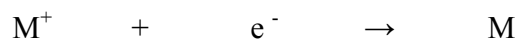
iii. Power Supply Unit

The power supply units can be of following types

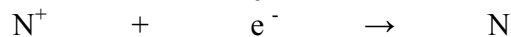
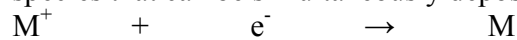
- Direct current at constant current which lead to galvanostatics deposition.
- Direct current at constant voltage which lead to potentiostatic deposition.
- Potentiostat providing pulsed deposition, potentiodynamic deposition.

Overall mechanism due to supply of power is as follows:

A current or voltage pulse applies an electric field so that M^+ ions would move to cathode. The elemental electro deposition process is as follows:



If electrolyte contain more than one ionic species that can be simultaneously deposited



As the electro deposition proceeds the ionic concentration in bath is depleted and has to be replenished by adding salt.[4]

2.3 Nature of Electrodeposition process

A common misconception about electrolysis is that "ions are attracted to the oppositely-charged - electrode." Ionic motion throughout the bulk of the solution occurs mostly by diffusion, which is the transport of molecules in response to a concentration gradient. Only the ions near to the interfacial region are likely to undergo migration.

2.4.1 Steps Involved in Electrodeposition Reaction

There are four steps that occur within 1-1000A⁰ from substrate.

- Ionic transport
- Discharge
- Breaking up of ion-ligand bond
- Incorporation of atoms on to the substrate followed by nucleation and growth

2.4.2 The various processes that occurs during electrodeposition:

i. Process that occur in electrolyte bulk

Ions that are sufficiently removed from the electrode surface can be move towards it under the influence of:

- Potential gradient $d\Phi/dx$ leading to ion drift.
- A concentration gradient dc/dx leading to diffusion of ions.
- Density convective current $d\rho/dx$. ρ is the density of electrolyte due to consumption of ions at the electrode.

The three terms contribution of migration, diffusion and convective current starts conversion process to mass transport toward the electrode.

ii. The process that occur near the electrode but within the electrolyte

Ionic species in the electrolyte are normally surrounded by a hydration sheath or some other complex forming ion or ligand present in electrolyte they move together as one entity and arrive near the electrode surface. Where the ion ligand system either accept electron from the cathode or donate electron to anode. This ionic discharge reaction occurs in electrolyte between 10 and 1000A⁰ from the electrode-electrolyte interfacial region.

iii. Process that occur on the electrode surface

The discharge ions arrive near the electrode where steps by step leading to the formation of new solid phase or growth of an electrodeposited film. The atoms thus deposited have a tender to form either an ordered conglomerate of crystalline phase or a disordered amorphous phase.

2.4 Influence of Cell Potential and pH on Deposition: (Stability diagrams):

In balancing redox equations, many electron-transfer reactions involve hydrogen ions and hydroxide ions. The standard potentials for these reactions therefore refer to the pH, either 0 or 14, at which the appropriate ion has unit activity. As, multiple numbers of H⁺ or OH⁻ ions are often involved, the potentials given by the Nernst equation can vary greatly with the pH. Hence, it is useful to look at the situation, by considering what combinations of potential and pH allow the stable existence of a particular species. This information is most usefully

expressed by means of an E-vs.-pH diagram, also known as a Pourbaix diagram.

Ex. Stability of water:

Water is subject to decomposition by strong oxidizing agents such as C₁₂ and by reducing agents stronger than H₂, with the parameters in shaded region in the fig. 3 below.[5]

The Reduction reaction: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$
OR

In neutral or alkaline solutions reduction reaction is $\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$

These two reactions are equivalent and follow the same Nernst equation which, at 25°C and unit H₂ partial pressure reduces to $E = E^\circ - (.059/2) \times 2 \text{ pH} = -0.059 \text{ pH}$

The Oxidation Reaction: $\text{H}_2\text{O} \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+ + 2\text{e}^-$

This reaction is governed by the Nernst equation which similarly becomes $E = 1.23 - 0.059 \text{ pH}$,

so the E-vs.-pH plots for both processes have identical slopes and yield the stability diagram for water as shown in Fig.(4).

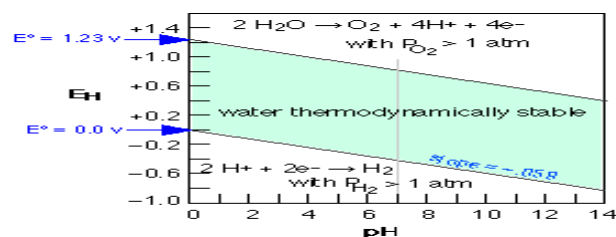


FIG.3 Stability (Pourbaix) diagram for water

The two E^o values shown at the left refer to "standard" conditions of unit H⁺ activity (pH=0) and gas pressures of 1 atm. At combinations of pH and E that lie outside the shaded area, the partial pressures of O₂ or H₂ exceed 1 atm., signifying the decomposition of water. The unity partial pressures are arbitrary criteria; in a system open to the atmosphere. Water can decompose even at much lower H₂ partial pressures, and at oxygen

pressures below 0.2 atm. Such diagram has relevance to electrochemical corrosion of metals. The metals above hydrogen in the activity series will tend to undergo oxidation (corrosion) by reducing H^+ ions or water.

Thus, in order to optimize the desired film characteristics, a good understanding of pourbaix diagram, electrode process and the process control parameters is necessary.

3. Conclusion

Electrodeposition is a promising competitor in thin-film preparation because of several advantages, such as the possibility for large-scale production, minimum waste of components, and easy monitoring of the deposition process. The use of electrode process control parameters in aqueous electroplating method is extremely important. The potential benefits of this include: brightening the deposit, increasing the grain size, changing mechanical and physical properties, reducing stress, reducing pitting, and

increasing the lifetime of deposition bath and deposits.

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