

Faculty of Science and Technology

M. Sc. (Physics)

Choice Based Credit System (CBCS)

To be implemented from Academic Year 2020-2021

Structure and Syllabus



SAVITRIBAI PHULE PUNE UNIVERSITY
GANESHKHIND, PUNE-411007

Proposed Structure of M. Sc. (Physics) Syllabus (C. B. C. S.)

1. Title of the Course: M. Sc. Physics

2. Preamble:

The curriculum for the M. Sc. (Physics) programme is designed to cater to the requirement of Choice Based Credit System following the University Grants Commission (UGC) guidelines. In the proposed structure, due consideration is given to Core and Elective Courses (Discipline specific - Physics), along with Ability Enhancement (Compulsory and Skill based) Courses. Furthermore, continuous assessment is an integral part of the CBCS, which will facilitate systematic and thorough learning towards better understanding of the subject. The systematic and planned curricula divided into two years (comprised of four semesters) shall motivate the student for pursuing higher studies in Physics and inculcate enough skills for becoming an entrepreneur.

Objectives:

- To foster scientific attitude, provide in-depth knowledge of scientific and technological concepts of Physics.
- To enrich knowledge through problem solving, minor/major projects, seminars, tutorials, review of research articles/papers, participation in scientific events, study visits, etc.
- To familiarize with recent scientific and technological developments.
- To create foundation for research and development in Physics.
- To help students to learn various experimental and computational tools thereby developing analytical abilities to address real world problems.
- To train students in skills related to research, education, industry and market.
- To help students to build-up a progressive and successful career in Physics.



3. Introduction: Semester Credit System

4. Eligibility: As per the rules and regulations published by SPPU, Pune.

5. Examination: As per the BOOKLET prepared by SPPU, Pune

- A. Pattern of Examination
- B. Standard of Passing
- C. ATKT Rules
- D. Award of Class
- E. External Students
- F. Setting of Question paper / Pattern of Question paper
- G. Verification / Revaluation

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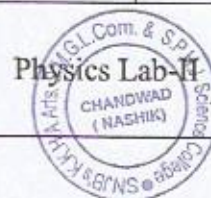
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Structure of M. Sc. Physics (Choice Based Credit System)

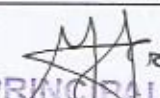
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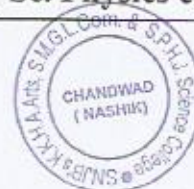
Subject Name	Year	Semester	Course Type	Course Code	Course Name	Credit				
Physics	I	I	Core Compulsory Theory Paper (CCTP)	PHCT-111	Mathematical Methods in Physics	4				
				PHCT-112	Classical Mechanics	4				
				PHCT-113	Electronics	4				
			Choice Based Optional Paper (CBOP-I)	PHOT-114	Choose any one from Group I	Theory	4			
				PHOP-114		Practical	0			
			OR							
			CBOP-I	PHOT-114	Choose any one from Group I	Theory	2			
				PHOP-114		Practical	2			
			Core Compulsory Practical Paper (CCPP)	PHCP-115	Physics Lab-I	4				
			II	CCTP	PHCT-121	Electrodynamics	4			
		PHCT-122			Atoms and Molecules	4				
		PHCT-123			Quantum Mechanics	4				
		CBOP-II			PHOT-124	Choose any one from Group I	Theory	4		
					PHOP-124		Practical	0		
		OR								
		CBOP-II			PHOT-124	Choose any one from Group I	Theory	2		
					PHOP-124		Practical	2		
		CCPP			PHCP-125	Physics Lab-II	4			



Year	Semester	Course Type	Course Code	Course Name		Credit	
2	III	CCTP	PHCT-231	Statistical Mechanics		4	
			PHCT-232	Solid State Physics		4	
			PHCT-233	Experimental Techniques in Physics - I		4	
		CBOP-III	PHOT-234	Special-I from Group II	Theory	4	
			PHOP-234		Practical	0	
		OR					
		CBOP-III	PHOT-234	Special-I from Group II	Theory	2	
			PHOP-234		Practical	2	
		CCPP	PHCP-235	Physics Laboratory - III		4	
		IV	CCTP	PHCT-241	Nuclear Physics		4
	PHCT-242			Experimental Techniques in Physics-II		4	
	CBOP-IV		PHOT-243	Choose any one from Group I	Theory	4	
			PHOP-243		Practical	0	
	OR						
	CBOP-IV		PHOT-243	Choose any one from Group I	Theory	2	
			PHOP-243		Practical	2	
	CBOP-V		PHOT-244	Special-II from Group II	Theory	4	
			PHOP-244		Practical	0	
	OR						
	CBOP-V	PHOT-244	Special-II from Group II	Theory	2		
PHOP-244		Practical		2			
CCPC	PHCP-245	Project		4			
Total credits of M. Sc. Physics course						80	



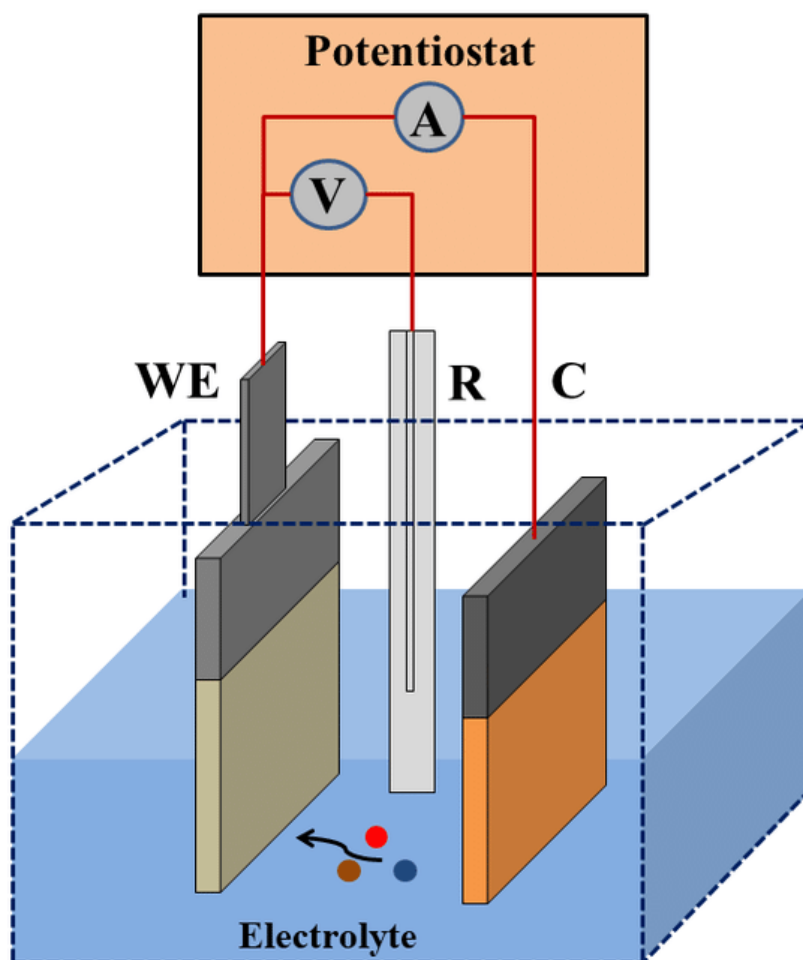

PRINCIPAL
 K.H.A. Arts, S.M.G.L. Comm.
 & S.P.H.J. Science College,
 Chandwad Dist. Nashik.



2020-2021

A project Report on

Electrochemical Deposition of Cu Thin Films



Student Name : Uzma Bano Mohammad Ishaque
Roll No : 17
Class : M.Sc- Physics
Guide Name : Prof. Dr.G.E Patil

Department of Physics



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and Shriman P. H. Jain Science College
Chandwad (Nashik)**



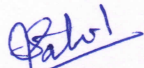
**S.N.J.B. Karmvir Keshavlalji Harakchandji Abad Arts
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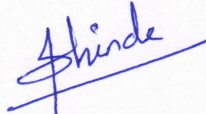
Certificate

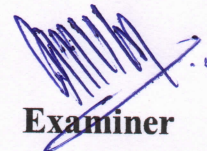
This is certify that, **Uzma Bano Mohammad Ishaque**, for the completion of
project titled

“Electrochemical Deposition of Cu Thin Films”

of M.Sc (Physics) for the academic year 2020-2021. She has completed her
project under the guidance of **Prof. Dr.G.E Patil**.


Project Guide


Head


Examiner

HEAD
Department of Physics
KKHA Arts, SMGL Commerce &
SPHJ Science College, Chandwad
Dist- Nashik 423 101 Maharashtra

Dr. G. E. Patil - A. B.

Acknowledgement

I am extremely happy to present this project report and would take this opportunity to express my feeling to those who guide, gave suggestion and helped me to make my project success.

I profess my heart full gratitude to my guide **Dr. G.E. Patil** for his valuable and friendly guidance, enagement and helpful suggestion throughout the progress of the research.

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Uzma Bano Mohammad Ishaque

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Chapter No. 1
Electrochemical Deposition of Cu Thin Films

Introduction:

Electrochemical deposition is a process by which a thin and tightly adherent desired coating of metal, oxide, or salt can be deposited onto the surface of a conductor substrate by simple electrolysis of a solution containing the desired metal ion or its chemical complex. A thin, metallic, inorganic or organic coating electrochemically deposited onto a conductor or semiconductor substrate has been used for more than a century to confer surface properties different from those of the base substrate with the aim either of protecting the substrate against corrosive and erosive attack by the surrounding environment or for decorative purposes, providing a particular appearance, such color and luster.

Process:

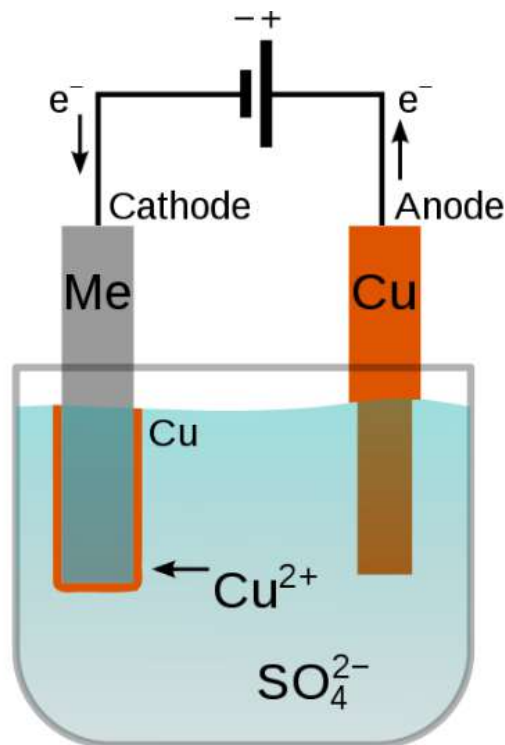


Fig-1: Electroplating of metal (Me) with copper in a copper sulfate bath

The cations associate with the anions in the solution. These cations are reduced at the cathode to deposit in the metallic, zero valence state. For example, for copper plating, in an acid solution, copper is oxidized at the anode to Cu^{2+} by losing two electrons. The Cu^{2+} associates with the anion SO_4^{2-} in the solution to form copper(II) sulphate. At the cathode, the Cu^{2+} is reduced to metallic copper by gaining two electrons. The result is the effective transfer of copper from the anode source to a plate covering the cathode.

The plating is most commonly a single metallic element, not an alloy. However, some alloys can be electrodeposited, notably brass and solder. Plated "alloys" are not true alloys, i.e. solid solutions, but rather discrete tiny crystals of the metals being plated. In the case of plated solder, it is sometimes deemed necessary to have a "true alloy", and the plated solder is melted to allow the Tin and Lead to combine to form a true alloy. The true alloy is more corrosion resistant than the as-plated alloy.

Many plating baths include cyanides of other metals (such as potassium cyanide) in addition to cyanides of the metal to be deposited. These free cyanides facilitate anode corrosion, help to maintain a constant metal ion level and contribute to conductivity. Additionally, non-metal chemicals such as carbonates and phosphates may be added to increase conductivity.

When plating is not desired on certain areas of the substrate, stop-offs are applied to prevent the bath from coming in contact with the substrate. Typical stop-offs include tape, foil, lacquers, and waxes. The ability of a plating to cover uniformly is called throwing power; the better the throwing power the more uniform the coating.

Process:

The electrolyte should contain positive ions (cations) of the metal to be deposited. These cations are reduced at the cathode to the metal in the zero valence state. For example, the electrolyte for copper plating can be a solution of copper(II) sulphate, which dissociates into Cu^{2+} cations and SO_4^{2-} anions. At the cathode, the Cu^{2+} is reduced to metallic copper by gaining two electrons.

When the anode is made of the coating metal, the opposite reaction may occur there, turning it into dissolved cations. For example, copper would be oxidized at the anode to Cu^{2+} by losing two electrons. In this case, the rate at which the anode is dissolved will be equal to the rate at which the cathode is plated and thus the ions in the electrolyte bath are continuously replenished by the anode. The net result is the effective transfer of metal from the anode source to the cathode.

The anode may instead be made of a material that resists electrochemical oxidation, such as lead or carbon. Oxygen, hydrogen peroxide, or some other byproducts are then produced at the anode instead. In this case, ions of the metal to be plated must be periodically replenished in the bath as they are drawn out of the solution. The plating is most commonly a single metallic element, not an alloy. However, some alloys can be electrodeposited, notably brass and solder. Plated "alloys" are not true alloys, i.e. solid solutions, but rather discrete tiny crystals of the metals being plated. In the case of plated solder, it is sometimes deemed necessary to have a "true alloy", and the plated solder is melted to allow the Tin and Lead to combine to form a true alloy. The true alloy is more corrosion resistant than the as-plated alloy. Many plating baths include cyanides of other metals (such as potassium cyanide) in addition to cyanides of the metal to be deposited. These free cyanides facilitate anode corrosion, help to maintain a constant metal ion level and contribute to conductivity. Additionally, non-metal chemicals such as carbonates and phosphates may be added to increase conductivity. When plating is not desired on certain areas of the substrate, stop-offs are applied to prevent the bath from coming in contact with the substrate. Typical stop-offs include tape, foil, lacquers, and waxes. The ability of a plating to cover uniformly is called *throwing power*; the better the throwing power the more uniform the coating.

Strike

Initially, a special plating deposit called a *strike* or *flash* may be used to form a very thin (typically less than 0.1 μm thick) plating with high quality and good adherence to the substrate. This serves as a foundation for subsequent plating processes. A strike uses a high current density and a bath with a low ion concentration. The process is slow, so more efficient plating processes are used once the desired strike thickness is obtained.

The striking method is also used in combination with the plating of different metals. If it is desirable to plate one type of deposit onto a metal to improve corrosion resistance but this metal has inherently poor adhesion to the substrate, a strike can be first deposited that is compatible with both. One example of this situation is the poor adhesion of electrolytic nickel on zinc alloys, in which case a copper strike is used, which has good adherence to both.^[3]

Electrochemical deposition

Electrochemical deposition has been widely used since the late 1990s for creating the copper conductive wires in advanced semiconductor devices. Pioneered by IBM, the technology was developed because previous methods for creating aluminum conductive wires in chips--via etching the metal lines and then filling in an insulating film with chemical vapor deposition and physical vapor deposition processes--would not work with copper because the metal is too hard to etch. Electrochemical https://www.ibm.com/blogs/research/2017/11/20years-cuwires/?mhsrc=ibmsearch_a&mhq=copper%20electroplating deposition of copper has generally now replaced aluminum CVD and PVD deposition processes for manufacturing conductive wiring in semiconductor chips for all of the most critical device layers.

Pulse electroplating

The pulse electroplating or pulse electrodeposition (PED) process involves the swift alternating of the electrical potential or current between two different values resulting in a series of pulses of equal amplitude, duration and polarity, separated by zero current. By changing the pulse amplitude and width, it is possible to change the deposited film's composition and thickness. The experimental parameters of pulse electroplating usually consist of peak current/potential, duty cycle, frequency and effective current/potential. Peak current/potential is the maximum setting of electroplating current or potential. Duty cycle is the effective portion of time in certain electroplating period with the current or potential applied. The effective current/potential is calculated by multiplying the duty cycle and peak value of current or potential. Pulse electroplating could help to improve the quality of electroplated film and release the internal stress built up during fast deposition. Combination of the short duty cycle and high frequency could decrease the surface cracks.

However, in order to maintain the constant effective current or potential, a high performance power supply may be required to provide high current/potential and fast switch. Another common problem of pulse electroplating is that the anode material could get plated and contaminated during the reverse electroplating, especially for the high cost, inert electrode such as platinum. Other factors that could affect the pulse electroplating include temperature, anode-to-cathode gap and stirring. Sometimes the pulse electroplating can be performed in heated electroplating bath to increase the depositing rate since the rate of almost all the chemical reaction increases exponentially with temperature per Arrhenius law. The anode-to-cathode gap is related to the current distribution between anode and cathode. Small gap to sample area ratio may cause uneven distribution of current and affect the surface topology of plated sample.

Brush electroplating

A closely related process is brush electroplating, in which localized areas or entire items are plated using a brush saturated with plating solution. The brush, typically a stainless steel body wrapped with an absorbent cloth material that both holds the plating solution and prevents direct contact with the item being plated, is connected to the anode of a low voltage direct current power source, and the item to be plated connected to the cathode. The operator dips the brush in plating solution then applies it to the item, moving the brush continually to get an even distribution of the plating material.

Brush electroplating has several advantages over tank plating, including portability, ability to plate items that for some reason cannot be tank plated (one application was the plating of portions of very large decorative support columns in a building restoration), low or no masking requirements, and comparatively low plating solution volume requirements. Disadvantages compared to tank plating can include greater operator involvement (tank plating can frequently be done with minimal attention), and inability to achieve as great a plate thickness.

Hard chrome in brush electroplating

Hard chrome is one of the most common plating materials used for hard plating and electroplating, due to its strength, resistance and sleek finish. However, chromium is very dangerous in its hexavalent state. When inhaled or consumed, airborne Cr^{6+} [JT2] has been linked to lung cancer and causes damage to the throat, mouth and nose.

This is because, in its hexavalent state, chromium has carcinogenic and teratogenic properties, which has a mutagenic effect on cells.

Every year, 558,000 US technicians are exposed to hexavalent chromium in the workplace, with those working in the electroplating, welding and painting industries are most at risk, due to increased exposure to high levels of Cr^{6+} compounds.

Because of the dangers linked to hexavalent chromium, finding safer, eco-friendly alternatives has been a main driver of brush electroplating research for the last decade. One alternative that has been developed is metal matrix composites (MMC). MMC offers unique and superior characteristics to metal plating solutions including hardness, wear resistance, and oxidation protection at high temperatures. This chrome alternative MMC includes cobalt chromium carbide, nickel tungsten carbide and nickel chromium carbide.

Barrel plating:

This technique of electroplating is one of the most common used in the industry for large numbers of small objects. The objects are placed in a barrel-shaped non-conductive cage, and then immersed in the chemical bath containing suspended atoms of the metal that is to be plated onto them. The barrel is then rotated, and electrical currents are run through the various pieces in the barrel which complete circuits as they touch one another. The result is a very uniform and efficient plating process, though the finish on the end products will likely suffer from abrasion during the plating process. It is unsuitable for highly ornamental or precisely engineered items.

Cleanliness:

Cleanliness is essential to successful electroplating, since molecular layers of oil can prevent adhesion of the coating. ASTM B322 is a standard guide for cleaning metals prior to electroplating. Cleaning includes solvent cleaning, hot alkaline detergent cleaning, electrocleaning, and acid treatment etc. The most common industrial test for cleanliness is the waterbreak test, in which the surface is thoroughly rinsed and held vertical. Hydrophobic contaminants such as oils cause the water to bead and break up, allowing the water to drain rapidly. Perfectly clean metal surfaces are hydrophilic and will retain an unbroken sheet of water that does not bead up or drain off. ASTM F22 describes a version of this test. This test does not detect hydrophilic contaminants, but electroplating can displace these easily since the solutions are water-based. Surfactants such as soap reduce the sensitivity of the test and must be thoroughly rinsed off.

Effects:

Electroplating changes the chemical, physical, and mechanical properties of the workpiece. An example of a chemical change is when nickel plating improves corrosion resistance. An example of a physical change is a change in the outward appearance. An example of a mechanical change is a change in tensile strength or surface hardness which is a required attribute in tooling industry.^[11] Electroplating of acid gold on underlying copper- or nickel-plated circuits reduces contact resistance as well as surface hardness. Copper-plated areas of mild steel act as a mask if case hardenings of such areas are not desired. Tin-plated steel is chromium-plated to prevent dulling of the surface due to oxidation of tin.

Electroplating, or electroless plating may be used as a way to render a metal part radioactive, by using an aqueous solution prepared from nickel-phosphorus concentrates which contain radioactive hypophosphite ^{32}P ions.

Electro deposition is categorized into the following three processes:

- (1) Electroplating
- (2) Electrophoretic deposition
- (3) Underpotential deposition

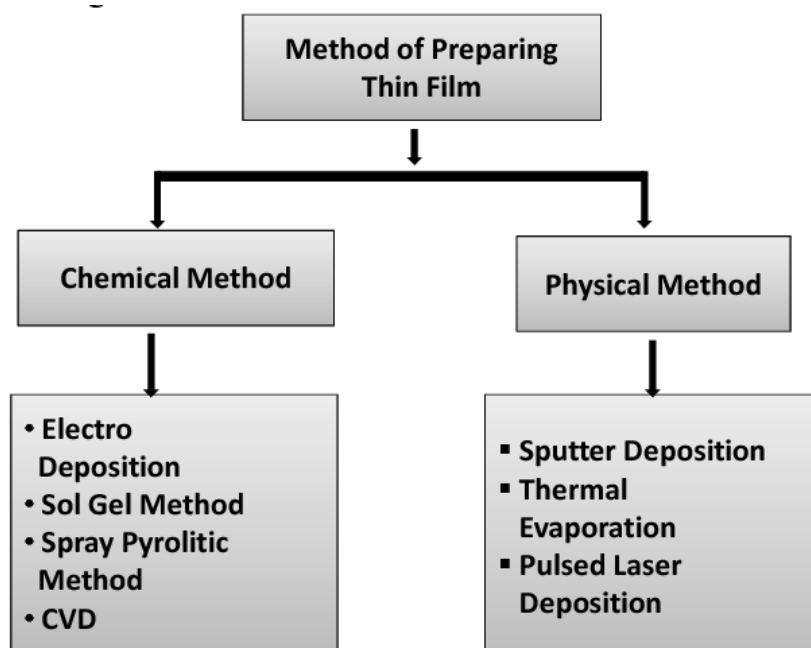
Applications of Electroplating:

Electroplating is primarily used to change the surface properties of an object (such as abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities), but may also be used to build up thickness on undersized parts or to form objects by electroforming.

Characterizations of thin films:

- XRD : X-ray powder diffraction
- SEM : *Scanning Electron Microscopy*
- TEM : Transmission Electron Microscopy
- EDS : Energy-dispersive X-ray spectroscopy
- CV: Cyclic Voltammetry
- FTIR :Fourier-transform infrared spectroscopy
- Raman Spectroscopy

Method of Preparing Thin Film:



Chapter No. 2

Introduction to Thin Films

Thin Films:

A **thin film** is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The controlled synthesis of materials as thin films (a process referred to as deposition) is a fundamental step in many applications. A familiar example is the household mirror, which typically has a thin metal coating on the back of a sheet of glass to form a reflective interface. The process of silvering was once commonly used to produce mirrors, while more recently the metal layer is deposited using techniques such as sputtering.

Advances in thin film deposition techniques during the 20th century have enabled a wide range of technological breakthroughs in areas such as magnetic recording media, electronic semiconductor devices, LEDs, optical coatings (such as antireflective coatings), hard coatings on cutting tools, and for both energy generation (e.g. thin-film solar cells) and storage (thin-film batteries). It is also being applied to pharmaceuticals, via thin-film drug delivery. A stack of thin films is called a multilayer.

In addition to their applied interest, thin films play an important role in the development and study of materials with new and unique properties. Examples include multiferroic materials, and superlattices that allow the study of quantum phenomena.

General Introduction:

Each material surface is exposed to various environmental influences. The surface of a solid body is subjected to corrosion and wear and interacts with light and electromagnetic fields. From the technological point of view the miniaturization of mechanic, electronic, optical and optoelectronic components permanently increases the surface to volume ratio of the involved materials. In modern material science specific surface properties therefore gain increasing importance.

Nonetheless, the desired mechanical, optical chemical or electronic properties are often opposed to the bulk properties which may be high mechanical stability, easy manufacturing or low material cost. Because of this fact a multitude of High Tech components are composite materials which mean that the surface properties significantly differ from the bulk properties. An example may be a mechanical part which has to exhibit high hardness (i. e. low wear under tribological load) as well as high fracture toughness (i. e. high resistance against crack propagation). One material alone may not fulfill these demands. The solution of the problem can be a composite material consisting of

a surface zone (coating) with high surface hardness and a tough bulk core. Other machine components as e. g. high temperature blades of gas turbines have to exhibit high temperature and corrosion resistance as well as high mechanical stability. Also in this case one property such as corrosion resistance can be provided by a modified surface or a coating while mechanical stability is given by the base material. Another large field of examples is constituted by thin film systems which act as laser mirrors, anti reflex coatings and other optically active surface modifications. In the optical industry they are deposited on substrates which guarantee mechanical stability and other specific properties. Thin films can also be found in optoelectronic, electronic and magnetic components which can only be manufactured because of the special physical properties of thin films which may deviate significantly from those of the bulk material. A prominent example for this case are hard disk read heads based on the Giant Magneto resistance effect (GMR) which only operate due to the special properties of a combination of magnetic and insulating thin films.

Definition of Terms

In the beginning the following definitions may be useful:

Substrate: Base material on of a film; (there may be, however, also free standing films!)

Film, Coating: Solid (or liquid) body which exhibits a significantly lower geometrical extension in one dimension than in the remaining two spatial dimensions. The properties of the film or coating have to differ significantly from the bulk.

Distinction: "Thin" Film - "Thick" Film: The limit between "thin" and "thick" films cannot generally be defined, although literature sometimes gives an arbitrary value of 1 μm . Basically, a film can be considered as "thin" when its properties are significantly different from the bulk. This can be due to:

1. the increasing surface to volume ratio at decreasing film thickness, and
2. the microscopic structure which is dependent on the deposition parameters

ad 1.: a low film thickness can cause the following effects : optical interferences, increase of the electrical resistivity and decrease of the temperature coefficient of electrical resistivity, increase of the critical magnetic induction and of the critical temperature in superconductivity, tunnelling of Cooper pairs (Josephson-effect). The film thicknesses which lead to the appearance of these thin film effects can be quite different. An Indium-Oxide film (In_2O_3), e. g., which can be used as temperature barrier coating due to its high transmission in the visible region and its high reflectivity in the infrared region (this is caused by optical interference effects) has to be approx. 300 nm thick.

For optical applications this film can be considered as thin. If the same material would serve as insulator in a Josephson junction, 300 nm would be much too thick to allow Cooper pairs to tunnel through the oxide. For this application the In₂O₃ film should have a thickness of only 2 nm. In other words: for one given application a film can be considered as "thin" while for another one the film can still be considered as "thick".

ad 2.: as a consequence of a microstructure which is different from the bulk (e. g. in respect to grain or crystallite size) the following effects may be observed: increase of corrosion resistance, increase of hardness, increase of the magnetic saturation induction, increase of the critical temperature of superconductivity, increase of the optical absorption. Structures like this are often metastable and can not only be achieved by thin film deposition methods, but also by many different methods of surface modification as there are electron beam, laser surface melting or ion implantation. In the latter case the "thin film" is a modified surface zone with properties significantly different from the bulk. Also in this case thicknesses range from few nm to several μm , and no definite distinction between "thin" and "thick" coatings may be justified.

Surface and Interface: In general, each border between well discernible phases is termed as "Interface". This can be the interface between a substrate and a film or between a coating and the environment, but also e. g. a grain boundary between two single crystalline grains in a solid. The term "Surface" is a sub quantity of the term "Interface" and designates the border between a solid or a liquid and gas or vacuum.

Film Deposition and Film Formation:

The deposition process of a film can be divided into three basic phases:

1. Preparation of the film forming particles (atoms, molecules, cluster)
2. Transport of the particles from the source to the substrate

3. Adsorption of the particles on the substrate and film growth These phases can - depending on the specific deposition process and/or on the choice of the deposition parameters - be considered as either independent or as influencing one another. The former is desirable since it allows to control the basic steps independently and therefore yields a high flexibility in the deposition process.

Applications of Thin Film Technology:

Engineering/Processing:

Tribological Applications:

Protective coatings to reduce wear, corrosion and erosion, low friction coatings

Hard coatings for cutting tools

Surface passivation

Protection against high temperature corrosion

Self-supporting coatings of refractory metals for rocket nozzles, crucibles, pipes

Decorative coatings

Catalysing coatings

Optics:

Antireflex coatings ("Multicoated Optics")

Highly reflecting coatings (laser mirrors)

Interference filters

Beam splitter and thin film polarizers

Integrated optics

Optoelectronics:

... Photodetectors

... Image transmission

... Optical memories

... LCD/TFT

Electronics:

- .. Passive thin film elements (Resistors, Condensers, Interconnects)
- ... Active thin film elements (Transistors, Diodes)
- ... Integrated Circuits (VLSI, Very Large Scale Integrated Circuit)
- ... CCD (Charge Coupled Device)

Cryotechnics;

- ... Superconducting thin films, switches, memories
- ... SQUIDS (Superconducting Quantum Interference Devices)

New Materials:

- ... Superhard carbon ("Diamond")
- ... Amorphous silicon
- ... Metastable phases: Metallic glasses
- ... Ultrafine powders (diameter < 10nm)
- ... Spheroidization of high melting point materials (diameter 1-500 μ m)
- ... High purity semiconductors (GaAs)

(Alternative) Energies:

- ... Solar collectors and solar cells
- ... Thermal management of architectural glasses and foils
- ... Thermal insulation (metal coated foils)

Magnetic Applications

- ... Audio, video and computer memories
- ... Magnetic read/write heads Sensorics
- ... Data acquisition in aggressive environments and media
- ... Telemetry
- ... Biological Sensorics Biomedicine
- ... Biocompatible implant coatings
- ... Neurological sensors
- ... Claddings for depot pharmaca

Deposition Methods - Overview

PVD (Physical Vapour Deposition)

Evaporation

Sputtering

Diode-system

Triode-system

Magnetron-system ("balanced/unbalanced")

Ion beam-system

Ionplating

DC-glow-discharge

RF-glow-discharge

Magnetron- discharge

Arc-discharge

Ion-Cluster-beam

Reactive versions of the above processes

CVD (Chemical Vapour Deposition)

Thermal CVD

Plasma-activated CVD

Photon- activated CVD

Laser-induced CVD

Plasmapolymerization

Electrochemical deposition

Cathodic deposition

Anodic oxidation

Elektrophoresis

Chemical deposition

Thermal Spraying

Flame

Explosion

Arc Plasma

Electro-Surfacing

Flame

Arc

Plasma

Laser

Plating

Casting

Rolling

Explosion

Rubbing

Deposition from the Melt

Deposition from Emulsions, Pastes

Mechanic

Thermal

Spray

Film Thickness and Deposition Rates

With the deposition methods described above a region in film thickness can be covered which reaches from less than 1 nm to several 10 mm. These are 6 to 7 orders of magnitude! The regions given in Fig. 1.1. and 1.2. are average values for films of good quality which can be deposited in reasonable times.

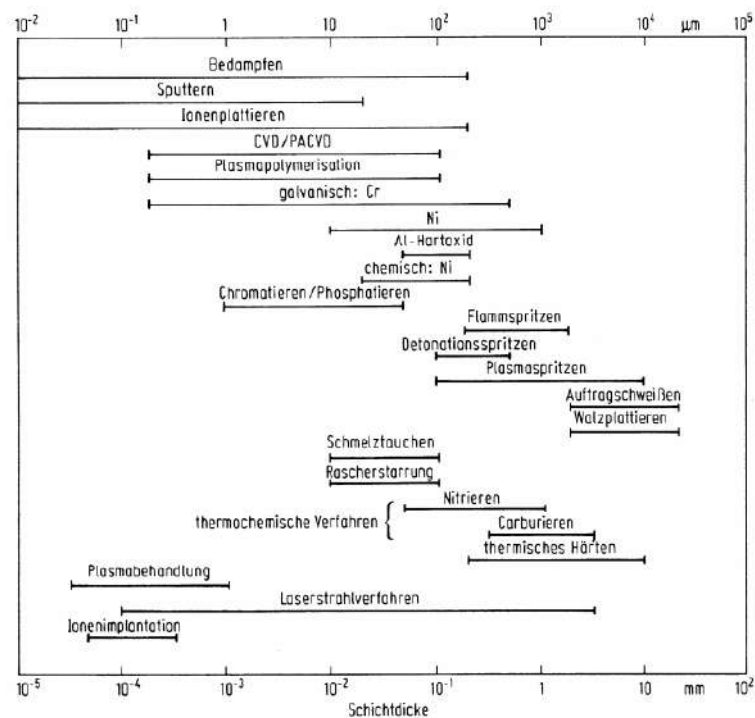


Fig. 1.1.: Film Thicknesses achievable by several deposition methods [1, p. 10] From Fig 1.1. and 1.2. it is also visible that methods based on spraying, plating and welding yield much higher thickness and rate than PVD, CVD or (electro)chemical methods. Abb. 1.2.: Deposition rates achievable by several deposition methods [1, p. 11]

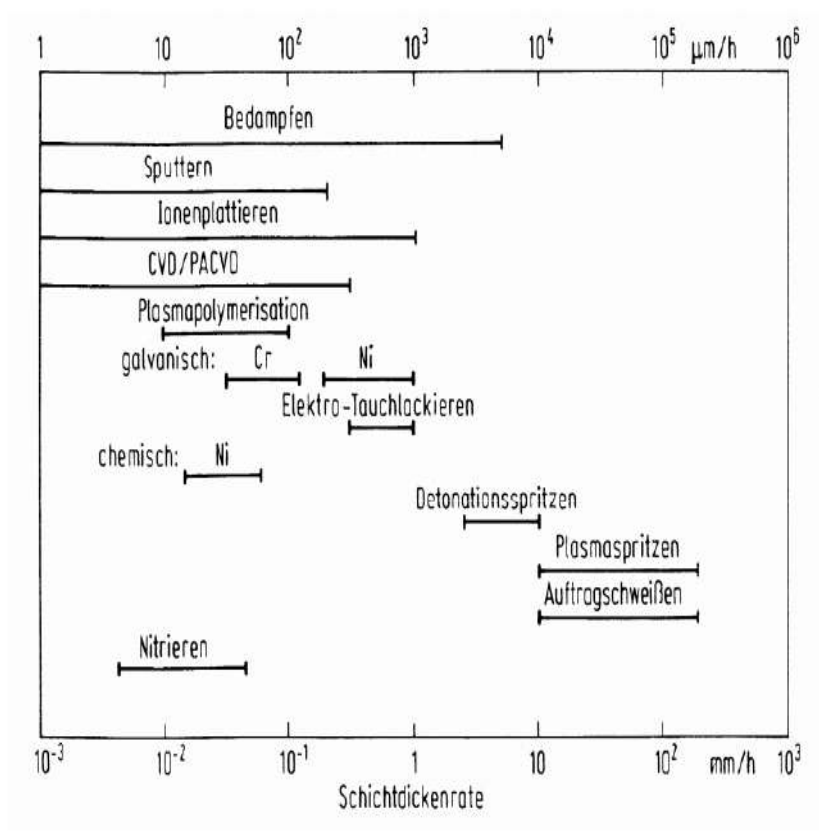


Abb. 1.2.: Deposition rates achievable by several deposition methods [1, p. 11]

Chapter No. 3

Study of Electrochemical Deposition Techniques

DEFINITIONS AND HISTORY:

Electrodeposition is an electrochemical process that allows the preparation of solid deposits on the surface of conductive materials. It is a commercially highly relevant process, providing the basis for many industrial applications, such as electro-winning, refining, and metal plating. Metal plating is the process that has perhaps the closest contact with most people's everyday life, because we are surrounded by things that have a protective or decorative coating, such as watches, buttons, belt buckles, doorknobs, handlebars, etc.

Additionally and more recently, as will be seen below, not only do the circuit boards and the packaging modules of computers, but also the recording and reading heads of their hard disk drives and the microprocessor chip itself may have plated material on them. Electrodeposits are formed by the action of an electric current passing in an electrochemical cell, a device that consists of two conductive or semi-conducting electrodes immersed in an electrolyte. The electrodes are called the working electrode (cathode), consisting of the object where electrodeposition is planned, and the counter-electrode (anode), necessary to complete the electrical circuit.

Electrolytes for electrodeposition are usually aqueous solutions containing positive and negative ions, prepared by dissolving metal salts. The electric current that flows between the two conductive electrodes in the presence of an external voltage is because of the motion of charged species, via migration and diffusion, towards the surfaces of the polarized electrodes. At the surface of the electrodes, the conduction mechanism must change from ionic to electronic, an interface process mediated by the occurrence of electrochemical reactions that promote the reduction or the oxidation (redox reactions) of the ionic species.

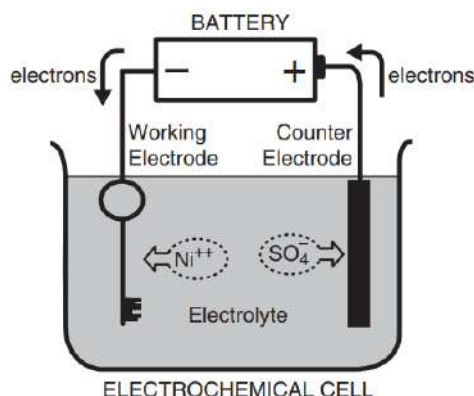


Fig. 1 Positively charged nickel ions in the electrolyte are attracted by the negatively charged key (working electrode). At the surface of the key they are reduced by gaining two electrons, and metal is deposited

An electrochemical cell with a battery is illustrated in Fig. 1, where the motion of the ions toward the electrodes is also sketched. In this case, the metallic salt NiSO_4 (nickel sulfate) dissolved in water is a practical example of an electrolyte for Ni-plating metallic objects. In this example, the object to be plated is a key, placed as the working electrode. By applying an external voltage with the negative terminal of the battery connected to the working electrode, the Ni^{2+} move to this electrode, where deposition takes place, and the SO_4^{2-} toward the positively charged counter-electrode. An essential characteristic of electrochemical reactions is that the exchange of charge does not occur between chemical species, as it does in a typical chemical reaction, but between chemical species and the electrode. The electrochemical reaction that is most important for the electrodeposition process is the one that occurs at the working electrode; i.e.,

for the example, in Fig. 1, it is the reduction reaction $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}^0$, where the Ni ions are reduced by receiving two electrons (e^-) from the electrode. At the counter-electrode, the oxidation of the sulfate radical is too energetic to occur, and the most probable oxidation reaction for inert electrodes in an aqueous electrolyte is the electrolysis of the water, forming H_2 and O_2 through the reaction $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2e^-$. This reaction occurs by donating two electrons to the anode, completing the electrical circuit and keeping the electric charge balanced.

Frequently used inert electrodes include platinum and glassy carbon. If the counter-electrode is a metallic bar or foil (a non-inert electrode), the electrodisolution of the metal could provide electrons for the electrode and ions for the solution. Historically, the discovery of electrodeposition is attributed to Luigi V. Brugnatelli, an Italian professor, who in 1805 was able to electrodeposit gold on the surface of a metallic object, from a solution containing dissolved gold, using a voltaic pile (battery). About 40 years later, John Wright, from Birmingham, England, discovered that potassium cyanide was a suitable electrolyte for gold and silver electroplating.

This discovery made electrodeposition an important commercial process for covering the surface of various kinds of metallic object with thin coatings of metals for corrosion protection and decorative purposes. Subsequently, baths for the deposition of other metals and alloys such as nickel, zinc, tin, and brass (an alloy consisting essentially of copper and zinc in variable proportions) were developed. For the next 100 years, the main idea was to use electrodeposition for covering the surface of inexpensive materials with a thin layer of a noble metal. By the 1940s, however, electrodeposition was rediscovered by the electronics industry. The electrodeposition of gold for

electronic components was a totally different kind of application of electrodeposition techniques. Over the years, electrodeposition became a highly developed process. Direct current (DC) power supplies were developed; anodic and cathodic reactions were described; new safer baths based on acid electrolytes, avoiding the earlier poisonous cyanide-based ones were discovered; models for the deposition process incorporating mass transport to the electrodes, charge transfer kinetics, and nucleation and growth at the working electrode were developed; and regulatory rules for waste water emission and waste disposal were created. Simultaneously, a gradual improvement in electrodeposition for large scale manufacturing processes took place.

ELECTRODEPOSITION APPARATUS AND CONCEPTS

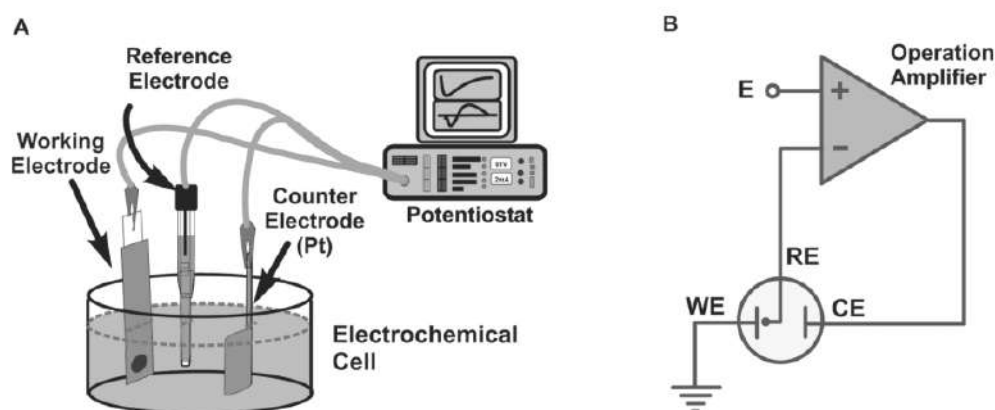


Fig. 2 (A) Electrochemical cell with three electrodes connected to a potentiostat. (B) Electronic sketch illustrating the mode of operation of a typical potentiostat.

Electrodeposition on the industrial scale requires an electrochemical cell and a DC current power supply. This approach is relatively simple and inexpensive, and is known as galvanostatic plating system, because the current between the electrodes is controlled (maintained constant). Another important deposition mode is the potentiostatic one. This mode is a consequence of the development of electrochemical science, where electrochemical reactions at the surfaces of electrodes are carefully investigated. The electrochemist developed reference electrodes, in order to measure the potential drop near the surface of electrodes.

Assuming that the electrolyte contains sufficient ions (has sufficiently high conductivity) to avoid any ohmic voltage drop, because of the resistance of the electrolyte between the electrodes, all the voltage applied by the battery (in Fig. 1) will appear near the surface of the electrodes, where a charged region is formed (usually named the double layer). It is very important to measure the

voltage drop across these charged regions, because it controls the driving force for phase transformation from ion to reduced state. A simple metal foil could be used as a reference electrode; however, because of the need to have a standard electrode to measure potential drops at the surface of different types of working electrode in contact with different electrolytes, a hydrogen electrode was elected, and now all electrode potentials are quoted relative to this arbitrarily chosen reference electrode. What is always measured is the potential difference between two electrodes.

By defining the potential of the hydrogen electrode as zero, it is possible to generate a table of all the possible redox reaction potentials relative to this electrode, and these potentials are called standard potentials. The standard hydrogen electrode (SHE), which is usually constructed by bubbling hydrogen gas over an immersed platinum foil, has its operation based on the redox reaction $\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\text{e}^-$.

Other reference electrodes that are robust, stable, and easily constructed than the SHE are frequently used in the laboratory, give potential measurements that can be converted to standard potentials by adding or subtracting a constant value. The most common are the calomel electrode ($\text{Hg}=\text{Hg}_2\text{Cl}_2$) and silver-silver chloride electrode ($\text{Ag}=\text{AgCl}$). The potential of an electrochemical cell, also known as the cell potential or electromotive force (emf) is the sum of the potential drops at the cathode and anode, where the reduction and oxidation reactions occur. With the introduction of a reference electrode the potentials of these two electrodes can be measured independently, allowing the independent investigation of the reactions that are taking place at each electrode (working or counter). These redox reactions are called half-cell reactions or simply half-reactions. The halfreaction potential E^0 can be measured with a SHE electrode at standard conditions, i.e., at electrolyte concentrations of 1 M, gas pressures of 1 atm., and temperature of 25°C, and tabulated.

Table 1 Standard electrode potentials in aqueous solution at 25°C

Cathode half-reaction	$E^0(\text{V})$
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.41
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.23
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$2\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l})$	0.17
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{SO}_4^{2-}(\text{aq})$	2.01

Note: aq., g and l denote aqueous, gas and liquid respectively.

Table 1 shows a set of standard potentials for cathode half-reactions. The introduction of the reference electrode led to a different experimental setup for electrochemical and electrodeposition experiments. Fig. 2(A) shows an electrochemical cell with three electrodes (working-, reference-, and counter-electrodes) and a potentiostat. The potentiostat is an electronic apparatus that maintains the potential difference between the working- and reference electrodes by controlling the potential difference between the working- and counter-electrodes. Fig. 2(B) shows a block diagram of the electronic circuitry of a potentiostat with an operational amplifier that keeps the voltage between reference electrode (RE) and working electrode (W) equal to the applied voltage E at the positive terminal, by regulating the cell potential between W and counter-electrode (CE).

By convention W is connected to ground. The three-electrode cell and the potentiostat enable the potentiostatic mode of deposition mentioned above. The potentiostatic mode means that the potential of the working electrode is kept constant during the experiment or deposition process, as depicted in Fig. 3A. An additional mode called pulsed deposition is also illustrated in Fig. 3B. In this mode, for pulsed potential, the potentiostat switches the working electrode potential between two values in order to have the potential varying as a square wave. For pulsed current deposition, a current source with a square wave output is sufficient. The three-electrode cell and potentiostat is also a powerful experimental tool for electrochemical investigations, permitting the implementation of different techniques, such as voltammetry. This technique consists of applying a potential ramp to the working electrode, which is achieved by applying a potential ramp to the positive terminal of the operational amplifier [of Fig. 2(B)], and measuring the resultant cell current. When the applied potential starts at a defined level and comes back to the same value after a period of time, the technique is called cyclic voltammetry.

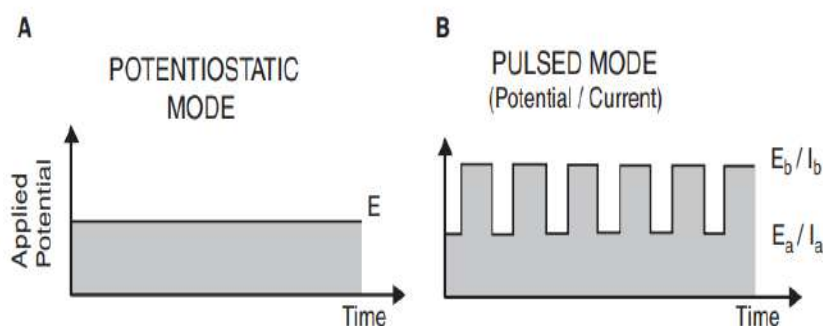


Fig. 3 Illustration of the potential as a function of time for potentiostatic and pulsed deposition modes.

When the applied potential starts at a level 1 and goes to a level 2, the resulting plot of the current versus the potential, is called a polarization curve or simply voltammogram. Fig. 4(A)

illustrates a potential ramp applied to the working electrode, and Fig. 4(B) the corresponding plot for the variation of the cathodic current as a function of the cathodic potential. This figure shows a typical polarization curve for the reduction of a metal at a conductive electrode. The onset of current, indicated by an arrow, corresponds to the minimum cathodic potential at which the reaction occurs (a fundamental value for electrodeposition purposes), the peak corresponds to the maximum current at a given rate of change of potential (also known as the reduction peak), while the third characteristic feature of the plot is the saturation of the current at more negative potentials. The intensity of the reduction peak depends on the potential scan-rate, this peak being not observed, in many cases, because of other reactions that occur simultaneously.

Potentiostatic Deposition:

This section will describe the potentiostatic mode using an electrolyte containing cobalt sulfate. By applying a potential ramp it is possible to obtain the polarization curve shown in Fig. 5(A). In this figure the onset of Co reduction is about 0.8 V. By selecting a deposition potential negative than this value, it is possible to obtain a deposit. Fig. 5(B) illustrates a Co deposit that is very homogeneous, apart from a microscopic defect because of a hydrogen bubble, obtained at a deposition potential of 1.1 V. Fig. 5(C) shows a plot of the deposition current. This plot, known as a current transient, gives information about the deposition process and allows the calculation of the electrodeposited charge from the area below the curve.

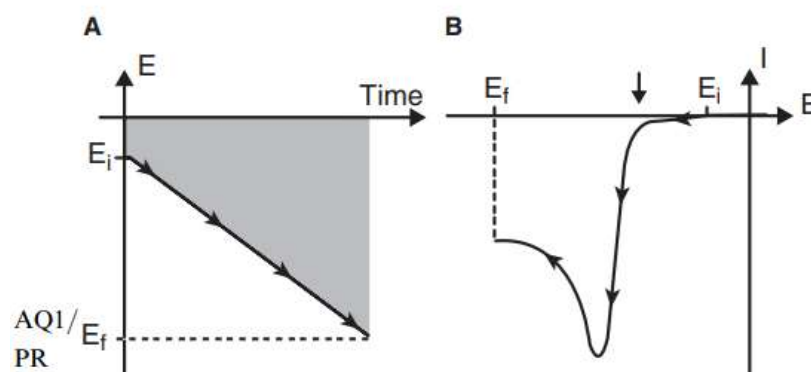


Fig. 4 Illustration of the applied potential ramp (A) to obtain a typical polarization curve (voltammogram) of metal deposition on a metal working electrode.

Factors influencing electrodeposition process

The process of metal deposition is affected by

- (1) current density (2) temperature
(3) hydrodynamic conditions (4) pH of the solution (5) nature of the metal (6) bath composition (7) addition agents (8) crystallography (9) impurities present in the solution.

1. Current density

Generally increase in current density decreases the crystal size. With increase in current density, the rate of formation of nuclei will be increased and the crystal size is decreased [8]. Increase in current density produce spongy or burnt deposits that usually contain hydroxides or basic salts. The concentration of the metal (and that of metal ions) in the diffusion layer decreases and the polarization increases while increasing the current density. The limiting current density in a given solution has been used to compute the composition and thickness of the diffusion layer and vice versa.

2 Temperature

In general, an increase in bath temperature causes an increase in the crystal size. Increase in bath temperature increases solubility and thereby the transport number, which in turn leads to increased conductivity of the solution. It also decreases the viscosity of the solution, thereby replenishing the double layer relatively faster. High bath temperature usually decreases less adsorption of hydrogen on the deposits and thereby reduces stress and tendency toward cracking.

3 Agitation

In general, agitation of the plating solution replenishes metal salts or ions at the cathode and reduces the thickness of the diffusion layer. It sweeps away the gas bubbles, which may otherwise cause pits. Agitation helps increasing the operating current density and thereby permits a higher operating current density.

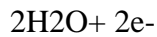
4 pH of the solution

pH control to maintain process optimization is a vital parameter in a plating operation. pH of the bath influences the hydrogen evolution voltage, the precipitation of

basic inclusion, the decomposition of the complex or hydrate from which the metal is deposited, and the extent of adsorption of additives. In a complex bath, pH may influence equilibrium between various ligands process. When the anode is insoluble, oxygen evolution takes place at the anode



+ e On the other hand, hydrogen evolution at the cathode is accompanied by the production of hydroxide ion:



In a neutral bath, if the current efficiency is greater at the anode than at the cathode, the bath becomes more alkaline. If the electrode efficiencies are similar, the pH of the bath remains unchanged. Hence change in pH of a plating bath is a good indication of electrode efficiencies. In certain conditions precipitation of metal hydroxides may occur locally within the cathodic double layer, which get codeposited with the plated metal and give defective deposit while increasing the pH due to hydrogen evolution. Thus buffers are necessary to minimize these pH changes.

5 Nature of the metal

Based on the magnitude of polarization, metals can be classified into three groups. Group I consists of metals like Ag, Pb, Cd, Sn etc., which are deposited at an overpotential of a few milli volts and rough deposits are obtained with grain size greater than 10^{-3} cm. Group III consists of metals like Ni, Co, Fe etc., which are associated with a large electrochemical polarization and are deposited as dense deposits with the grain size of around 10^{-5} cm. Cu, Bi, and Zn constituting the II group are intermediate metals with respect to the overpotential value and grain size of the deposit. The interaction of the substrates with the deposited metal differs and this affect the kinetics of nucleation and hence the number of grains per unit area [9].

6 Nature of the electrolyte and bath composition

The nature of the electrolyte has a significant effect on the properties of the deposit. In general, metal deposits obtained from simple salts are rough and coarse grained. Complexing anions and ligands generally shift the equilibrium potential to more negative values by reducing the activity of the free ions. This results in fine-grained

deposits with fewer tendencies to form dendrites.

Most of the metals used in plating can be deposited from more than one type of bath, each of which may be suited for a certain applications. In each type of bath, there is a fairly wide range of composition and concentration. Generally an increase in the metal concentration under given conditions decreases the cathode polarization, and as predicted, increases the crystal size. But the additives in a plating solution play a more important role in the crystal size and its distribution.

7 Addition agents

Addition agents are substances, which are intentionally added to metal depositing solutions in small quantities to produce a beneficial change in the properties of the deposit [10]. Generally their effects seem to be out of proportion to their concentration [11]. Additives affect deposition and crystal building processes as adsorbates at the surface of the cathode. There are two basic types of adsorption: chemisorption and phisorption. Adsorbed additives affect the kinetics of electrodeposition and the growth mechanism by changing the concentration of growth sites on a surface, the concentration of adions on the surface, the diffusion coefficient D , and the activation energy of surface diffusion of adions. These addition agents decrease the interfacial tension at the metalsolution boundary due to adsorption on the surface resulting in the reduced grain size of the crystals [12].

In electrodeposition process additives can be added in the form of leveling agents, stress reliever, wetting agent and brighteners. Leveling agent is added to reduce the surface roughness during deposition. Theories of leveling are based on (i) the correlation between an increase in the polarization produced by the leveling agents, [13] (ii) preferential adsorption of leveling agent on high point (peak or flat surfaces) (iii) and inhibition of deposition at these points [14,15]. Stress relievers are selectively adsorbed or occluded and change the crystal orientation and reduce the stress [16]. Wetting agents are used to wet the 'cathode surface' although in practice, their role is to reduce the surface tension of water so that hydrogen bubbles may more easily get detached from the surface. Brightener modifies the deposits by preferential surface adsorption. There are three possible mechanisms for bright deposition: (i) diffusion-controlled leveling (ii) grain refining (iii) randomization of crystal growth [17].

8 Crystallisation process

There are two basic types of formulation of coherent deposits [14, 18] Viz., layer growth and three dimensional (3D) crystallites growth (Figure 1.2). In the layer growth mechanism a crystal enlarges by a spreading of discrete layers (steps), one another across the surface. In this case growth layer, a step, is a structure component of coherent deposit. Steps, or growth layers, are the structural components for the construction of a variety of growth forms in the electrodeposition of metals. (E.g., columnar crystals, whiskers and fiber texture). Many monoatomic steps can unite (bunch, coalesce) to form a polyatomic step.

In the 3D crystallites growth mechanism the structural components are 3D crystallites, coherent deposit is built up as a result of coalescence of these crystallites. The growth sequence of electrodeposition via nucleation coalescence consists of four stages: (1) formation of isolated nuclei and their growth to TDC (3D crystallites), (2) coalescence of TDC, (3) formation of linked network, and (4) formation of continuous deposit. The difference in crystal structure during deposition stems from the potential dependence of the nucleation and growth processes. Competition between nucleation and growth processes is strongly influenced by the potential of the cathode [19].

8.1 Development of columnar microstructure

The columnar microstructure is perpendicular to the substrate surface, as shown in figure.1.2. This microstructure composed of relatively fine grains near the substrate but then changes to a columnar microstructure with much coarser grains at greater distances from the substrate. The low surface energy grains grow faster than the high-energy ones. This rapid growth of the low-surface-energy grains at the expense of the high-energy grains results in an increase in mean grain size with increased thickness of deposit and the transition from a fine grain size near the substrate to a coarse, columnar grain size.

9 Effect of impurities and their control

Similar to the action of addition agents, impurities in the plating solution have significant effect on the performance of the plating solution and on the properties of the plated coatings [20]. Organic impurities, introduced into the plating solution as surface greases or lubricants or breakdown products of addition agents, can be easily removed by Substrate

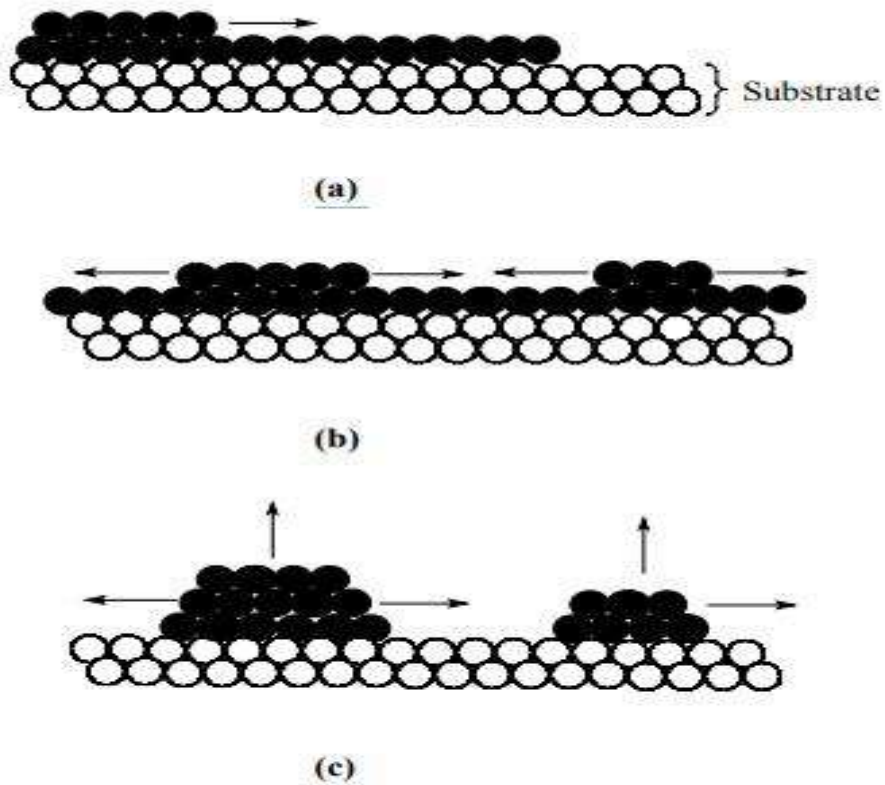


Figure 1.2 Schematic representation of layer growth (a, b) and the nucleation-coalescence mechanism (c)

treatment with activated charcoal. Metallic impurities cause major problem and can be removed by dummy electrolysis. These impurities reduce the current efficiency, quality and alter the growth morphology.

Chapter No. 4

Characterization of Thin Films

Introduction

In the past years the advancement in science has taken place mainly with the discovery of new materials. Characterization is an important step in the development of exotic materials. The complete characterization of any material consists of phase analysis, compositional characterization, structural and surface characterization, which have strong bearing on the properties of materials. In this section different analytical technique used to characterize our thin films are described with relevant principles of their operation and working.

Electrochromic Characterization Techniques:

Electro analytical techniques are concerned with the measurement of time related electrical quantities, such as charge or current and potential their relationship to the chemical reactions concerned.

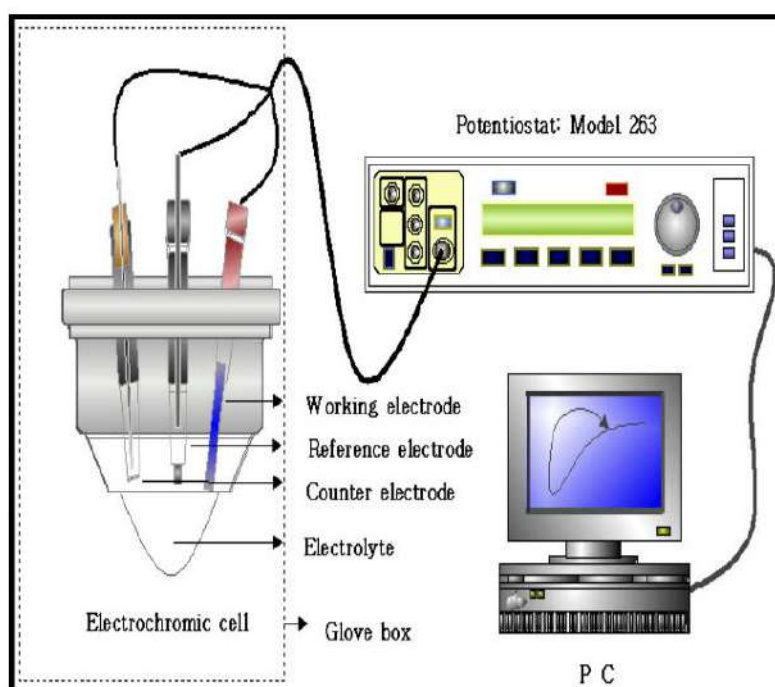


Fig. 2.B.1 Schematic diagram of the EC cell apparatus prepared for EC property measurements.

Commercial Potentiostat CHI 400 electrochemical Analyser can be used for electrochromic characterizations of thin films.[28,29]The measurements requires an electrochemical cell with the three electrodes namely working, counter, and the reference, versus which the electrode potential are measured.

Cyclic voltammetry (CV) and Linear sweep techniques (LSV)

Cyclic voltammetry is often the first experiment performed in an electro analytical study. In particular, it offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect media upon the redox process. In cyclic voltammetry a reversible dc potential sweep (using a triangular potential waveform) was applied between working electrode (film) and counter electrode and resulting current response versus a reference electrode (SCE) is measured.

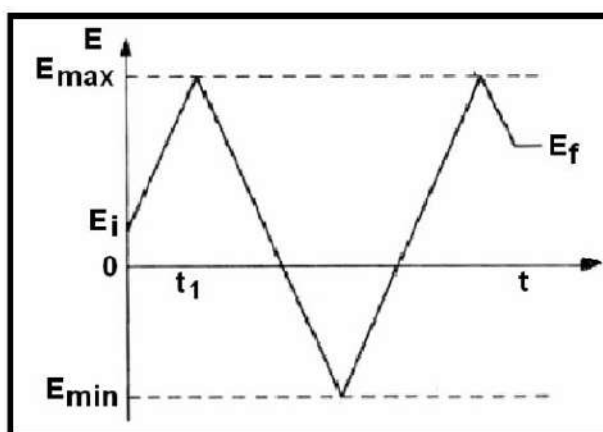


Fig.2.B.2 Variation of Applied Potential for Cyclic Voltammetry

In cyclic voltammetry, on reaching $t = t_1$ the sweep direction is inverted as shown in figure 2.B.2 and sweep until E_{min} , then inverted and sweep to E_{max} etc. The important parameters involved are • The initial Potential E_i • The initial sweep direction • The sweep rate v • The maximum potential, E_{max} The minimum potential, E_{min} • The final Potential, E_f

The kinetics of electrode reactions does not measure the rate of electron transfer itself, as this is an adiabatic process, following Frank-Condon principle, and occurs in approx. 10-16s. What it measures is the time needed for the species, once they have reached the interfacial region, to arrange themselves and their ionic atmospheres into position for electron transfer to be able to occur. According to kinetics of the reactions there are three types of reactions, 1. Reversible 2. Irreversible 3. Quasi reversible

A) Reversible system:

Fig. 2.B.3 shows a typical curve for linear sweep voltammetry (LSV) recorded for reversible reaction of the type $O + ne^- \rightarrow R$.

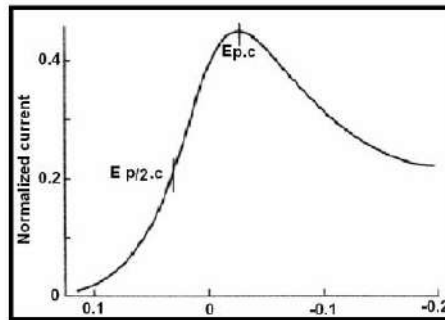


Fig. 2.B.3 A typical curve for linear sweep voltammetry (LSV)

The curve can be understood in the following way. On reaching a potential where the electrode reaction begins, the current rises as in a steady state voltammogram. However, the creation of a concentration gradient and consumption of electroactive species means that, continuing to sweep the potential, from a certain value just before the maximum value of the current, peak current, the supply of electroactive species begins to fall. Owing to depletion, the current then begins to decay, following a profile proportional to $t^{-1/2}$ which is shown in Fig.2.B.3, similar to application of potential step. Fig. 2.B.4 shows the typical cyclic voltammetry (CV) for reversible system.

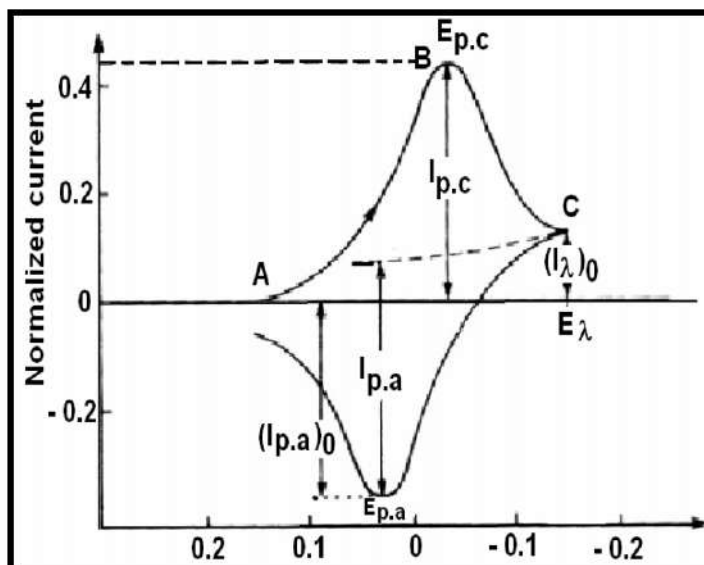


Fig. 2.B.4 The typical cyclic voltammetry (CV) for reversible system.

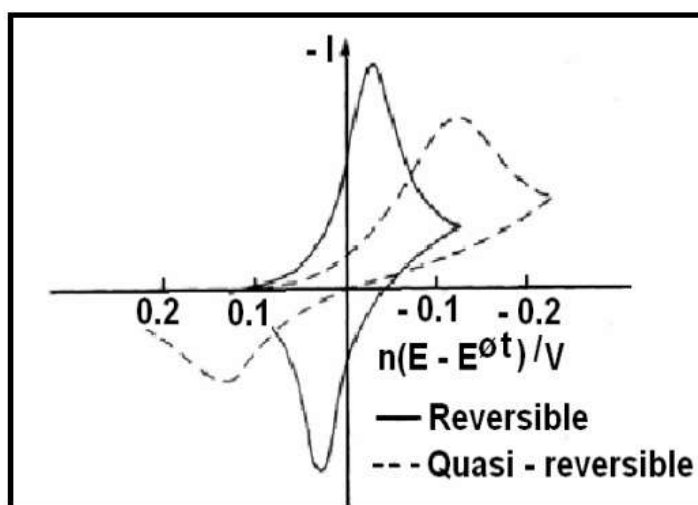
Another practical factor affecting the voltammogram is the solution resistance between working and reference electrode. This resistance leads to a shift in the potential of the working electrode by $i_p R\Omega$ where $R\Omega$ is the resistance (uncompensated) of the solution.

B) Irreversible system

In the case of an irreversible reaction of the type $O + ne^- \rightarrow R$, linear sweep and cyclic voltammetry lead to the same voltammetry profile, since no inverse peak appears on inverting the scan direction.

C) Quasi reversible systems

The extent of irreversibility increases with increase in sweep rate, while at the same time there is a decrease in the peak current relative to the reversible case and an increasing separation between anodic and cathodic peaks. On increasing sweep rate, there is less time to reach equilibrium at the electrode surface; reactions which appear as reversible at low sweep rates, can be quasi reversible at high sweep rates. Fig. 2.B.5 shows the effect of increasing irreversibility on the shape of cyclic voltammogram.



**Fig. 2.B.5 The effect of increasing irreversibility
on the shape of cyclic voltammetry**

Cyclic Voltammetry (CV) is the most widely used technique for acquiring qualitative information about electrochemical reactions taking place at the electrode - electrolyte interface. It offers a rapid location of redox potentials of the electroactive species in agitated or quiescent electrolyte and convenient evaluation of the effect of media upon the redox process[30-34]. In CV the

potential is continuously changed as a linear function of time in potential window + volts VS SCE and resulting current response is recorded. The resulting current versus potential plot is termed as a cyclic voltammogram. A smooth curve indicates that no well defined phase change occur during the reaction. It is assumed that only the oxidized ionic species are present initially, the mass transfer under concentration gradient is diffusion controlled and Fick's law of diffusion holds good for both oxidized and reduced ionic species. The redox potentials are predicted by Nernst equation given by,

$$E = E_o + (0.059 / n) \log (C_o / C_r) \quad \text{-----} \quad 2.1$$

Where, n = No. of electrons transferred

C_o and C_r = concentration of oxidized and reduced ionic species

During a negative potential scan (coloration) in the first half cycle, as the applied potential approaches the characteristic reduction potential (E_{pc}) predicted by Nernst equation, the cathodic current attains a peak value (I_{pc}). At least 90/n mV beyond the peak, the direction of applied potential is reversed. This helps in locating the presence of another reducible species in the bath. During the reverse positive scan (bleaching) the reduced ionic species get oxidized and with similar trend the anodic current a peak value (I_{pa}) at an oxidation potential (E_{pa}). If the redox reaction is reversible i.e. maintain the surface concentrations of oxidized and reduced species as per the Nernst equation, the voltammogram is symmetrical otherwise it is asymmetrical.

D) Diffusion Coefficient;

It is the measure of ease with which an ionic speices can intercalate /deintercalate in the host. It is given by Randles and Sevick equation

$$D^{1/2} = I_p / 2.69 \times 10^5 \cdot n^{2/3} \cdot C \cdot A \cdot V^{1/2} \quad \text{-----} \quad 2.2$$

I_p = Cathodic or anodic peak current

C = Concentration of ionic species

n = Ionic charge

A = Area of film

V = Potential scan rate

Pulse techniques

A step in applied potential or current represents an instantaneous alteration to the electrochemical system. Potential and current step give complimentary information because, where as in first case the potential causes a brief capacitive current peak, in second case a part of the applied current, the value of which probably vary with time, is always used to charge the double layer as the potential changes.

Potential Step:Chronoamperometry (CA)

The study of variation of the current response with time under potentiostatic condition is chronoamperometry [35]. The current resulting from a potential step from a value of the potential where there is no electrode reaction to one corresponding to the mass transport limited current was calculated for simple system $O + ne^- \rightarrow R$, where only O or only R is initially present. This is the faradic current, If since it is due only to faradic electrode process (only electron transfer). In the present study we have used double potential step chronoamperometry to measure the speed of electrochromic response and to apprehend intercalation and de-intercalation. An overview of CA experiment is shown in figure. The potential is altered between two values. We consider an initial step from a potential where there is no electrode reaction to a value to the limiting reduction current (only O initially present in solution); at $t = \tau$ the potential reverts to its initial value and there is oxidation of R that was produced. As mass transport under these conditions is solely by diffusion, the i - t curve reflects the change in the concentration gradient in the vicinity of the surface. This involves a gradual expansion of the diffusion layer associated with the depletion of the reactant and hence decreased slope of the concentration profile as time progresses. Accordingly, the current decays with the time (Fig.2.B.6) as given by Cottrell equation (2.3).

$$I_f(t) = \frac{nFAD^{1/2}c_\infty}{(\pi)^{1/2}} \dots\dots\dots (2.3)$$

It indicates the decrease of the current with $t^{1/2}$, which is shown in Fig.2.B.6. Such a $i(t^{1/2})$ constancy is often termed a "Cottrell behavior"

The time required for the transition from colored to bleached state or vice-versa under the application of voltage pulse is termed as response or switching time. Though the magnitude of

response time depends upon end use demand, a minimum switching time is necessary in advanced opto-Electronic EC devices.

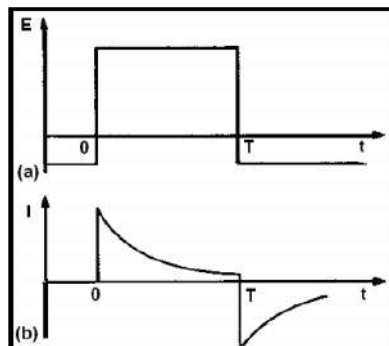


Fig. 2.B.6 Chronoamperometric plot exhibiting I Vs t behavior

Chapter No. 5

Advantages, Disadvantages & Applications

Advantages:

- Corrosion resistance: a corrosion-prone substance such as iron can be coated with a layer of non-corrosive material, thereby protecting the original material.
- Decorative items: shine and luster can be imparted to otherwise dull surfaces. This makes for great decorative items.
- Cheaper ornaments: instead of making ornaments out of gold or silver, one can make them using cheaper metals and electroplate the ornaments with gold. This reduces the cost of ornaments greatly.
- Improving mechanical characteristics: electroplating can also improve the mechanical characteristics of metals.
- They allow growing functional nanoparticles through complex 3D nano templates.
- This can be performed within a nonporous membrane which serves to act as a template for nanoparticle growth.
- Applicable at room temperature from water based electrolysis.
- These methods are suitable to scale down to the deposition of a few atoms or up to large dimensions, film thickness could range from 1nm to 10 microns etc.

Disadvantages:

- Non-uniform plating: electroplating may or may not be uniform and this may result in a substandard appearance of the plated material.
- Cost: the process is costly and time consuming.
- Pollution potential: the electroplating solution, after use, needs to be disposed off safely and is a cause of environmental concern.
- Pollutants from electroplating industry are dangerous.
- This process uses harmful chemicals that can result in death.
- The disposal of waste products produced during the process of electroplating is a major problem. The waste conducting solution pollutes the environment.
- The process requires multiple coating of the metals, which is time consuming.
- The cost of setting up the apparatus is high.

Applications:

- They are used to make nanocrystalline metals, alloys and composite materials.
- They are used for the production of dendritic hierarchical structure and many well ordered transition metal oxide, hydroxides and sulfides.
- They are used in jewelry making to coat base metal with precious metals to make them more attractive and valuable and sometimes more durable.
- They are used to increase wear resistance.
- They are used to protect against surface abrasions.
- They are used to reduce friction.
- They are used to improve electrical conductivity.
- They are used to prepare surface for better adhesion before painting and recoating.
- They are used to make material brittle stronger and more durable.
- They are used in magnetic applications such as the manufacturing of computer hard drives.
- They are used for providing an undercoating that facilitates adhesion with additional coatings etc.

Chapter No. 6

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Attendance Workshop/Conference:





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Certificate of Participation

This is to certify that Mr./Miss Uzma Bano Mohammad Ishaque
for his/her successful participation in 12th INFINITY Physics Project Online
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This is to Certify that, **Miss Uzma Bano Mohammad Ishaque** of
S. N. J. B & S. P. H Jain Science College of Chandwad, 423101,

participated in the workshop on "Astronomy and Astrophysics" organized by
Department of Physics and IQAC on 20th & 21st August, 2020.

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Your Faithfully,

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