

CHAPTER - 1

****THIN FILM DEPOSITION TECHNIQUES -A REVIEW***

1.1. INTRODUCTION

Thin film technology has become extremely important today for fundamental studies in many fields of physics, electronics, and chemistry and is also employed in numerous practical applications. The tremendous progress in the field of thin film physics has been stimulated and widened to a large degree by the recent development of most efficient high and ultra-high vacuum systems up to many feet in diameter in which thin films can be deposited with great ease by the high vacuum evaporation technique. In addition, new instrumentation for measuring pressure, gas composition, and deposition rates during the evaporation, and novel evaporation sources, which are often automatically controlled, now permit the preparation of thin films under precisely controlled and completely reproducible conditions.

Some workers use such films to obtain information about the properties of solids in general, since certain measurements can be made more conveniently using thin films. Others are more interested in fundamental properties of solids in thin film forms, since these may differ considerably from those of the bulk material. Examples of such research include studies of the optical, electrical, magnetic and superconducting properties, investigations of structural order, dislocation, migration phenomena and phase transitions, and of various surface reactions and surface phenomena. The results obtained by such fundamental studies are also of great interest to those concerned with the practical and commercial applications of thin films. Examples of such applications which are most important for the fields of optics and electronics are: highly reflecting mirror coatings, protective layers, antireflection films, beam-splitters, reflection and transmission type interference filters with narrow and wide band widths, polarizer; radiation

detectors, coatings for image-forming devices, light intensifiers, and solar energy converters, surface films for controlling the temperature of satellites, for passive and active electronic device film components, thin film circuits, and superconducting thin film devices [1].

Thin films form when it is built up as a thin layer of solid substance on a solid support called the substrate by controlled condensation of the individual atomic, molecular or ionic species, either directly by a physical process, or via a chemical and/or electrochemical reaction.

We present in this chapter a brief review of different deposition techniques. Though thin film deposition techniques are discussed in detail in various standard books [2], it is discussed here in brief to place the deposition methods described in the present work (dip deposition technique and open air chemical vapour deposition technique) in their proper perspective.

A thin film deposition process involves three basic steps: (i) creation of atomic/molecular/ionic species, (ii) transport of these species through a medium (vapour, stream or spray/ or liquid) and (iii) condensation of the species on a substrate. Depending on whether the vapour species has been created by a physical process (such as thermal evaporation and sputtering) or by chemical or electrochemical means, the thin film deposition processes can broadly be divided into two classes.

- (i) Physical Methods of deposition or Physical Vapour Deposition (PVD) and
- (ii) Chemical Methods of deposition.

By combining these two methods, hybrid techniques such as reactive evaporation/sputtering and plasma deposition have been developed.

Although genuine differences exist between the two classes, the line of demarcation is not really sharp and in many cases the techniques involve features of both classes; nevertheless, the two are discussed separately.

1.2. PHYSICAL VAPOUR DEPOSITION (PVD)

As already stated, PVD techniques are those where vapour of the materials to be deposited has been created by a physical process, mainly based on evaporation and sputtering.

1.2.1. Evaporation technique: The evaporation of a material requires heating to a sufficiently high temperature to produce the desired vapour pressure. The vapour atoms traverse the medium and are made to condense on a substrate surface to form a thin film. The rate of condensation/deposition of the vapour atoms depends on the vapour-source-substrate geometry and the condensation co-efficient on the surface under given physical conditions.

Among the evaporation techniques thermal evaporation is comparatively simple and very convenient. In this method, solid material vaporizes when heated to a sufficiently high temperature and then the condensation of the vapour onto a cooler substrate, yields thin solid films. This is achieved by carrying out the deposition in a vacuum of such magnitude that the mean free path of the ambient gas molecules is greater than the dimensions of the deposition chamber and the source - substrate distance. Because of collisions with ambient gas atoms, a fraction of the vapour atoms proportional to $e^{-d/l}$ will be scattered. Here 'd' is the distance during their transfer through gas and 'l' is the mean free path and its value at 25° C is about 450 cm at 10^{-5} Torr. Other evaporation techniques such as vacuum evaporation, arc evaporation, co-evaporation, flash evaporation, laser evaporation, electron-beam evaporation, activated reactive evaporation (ARE) are also commonly used for the deposition of thin films. A variety of sources is used to evaporate different materials, depending on whether they are available in wire, foil or powder form.

Figure 1.1 shows a few evaporation techniques which are commonly used for the deposition of thin films. Flash Evaporation [Fig.1.1.(a)], a rapid evaporation of a multicomponent alloy or compound, which tends to distill fractionally, may be obtained [3,4] by continuously dropping fine particles of the materials onto a hot surface so that numerous discrete evaporations occur. It has been used for preparing films of ceramics [5], Bi_2Te_3 [6], III-V compounds [7] etc.

In Arc Evaporation [Fig.1.1.(b)], by striking an arc between two electrodes of a conducting material, sufficiently high temperatures can be generated to evaporate refractory materials such as Nb and Ta. It is widely used for evaporation of carbon for electron-microscope specimens.

The Exploding-Wire techniques [Fig. 1.1.(c)], consists of exploding a wire by a sudden resistive heating of the wire with a transient high current density (approx. 10^6 A/cm²). It is achieved by discharging a bank of condensers (~ 10 to 100 μF), charged to a voltage ~ 1 to 10 KV, through a metallic wire.

In case of Laser Evaporation, the enormous intensity of a laser may be used to heat and vaporize materials by keeping the laser source outside the vacuum system and focusing the beam onto the surface of the materials to be evaporated [Fig. 1.1(d)].

The evaporated films are generally not uniform because the amount of the material reaching the substrate depends on the angle (θ) between source and the substrate area [8]. The rate of deposition follows a $\text{Cos}\theta/r^2$ variation for a point source and $\text{Cos}^2\theta/r^2$ variation for evaporation from a small area, r being the distance between the source and the substrate. By proper selection of source, source-substrate geometry and substrate rotation, it is possible to get highly uniform films over large areas.

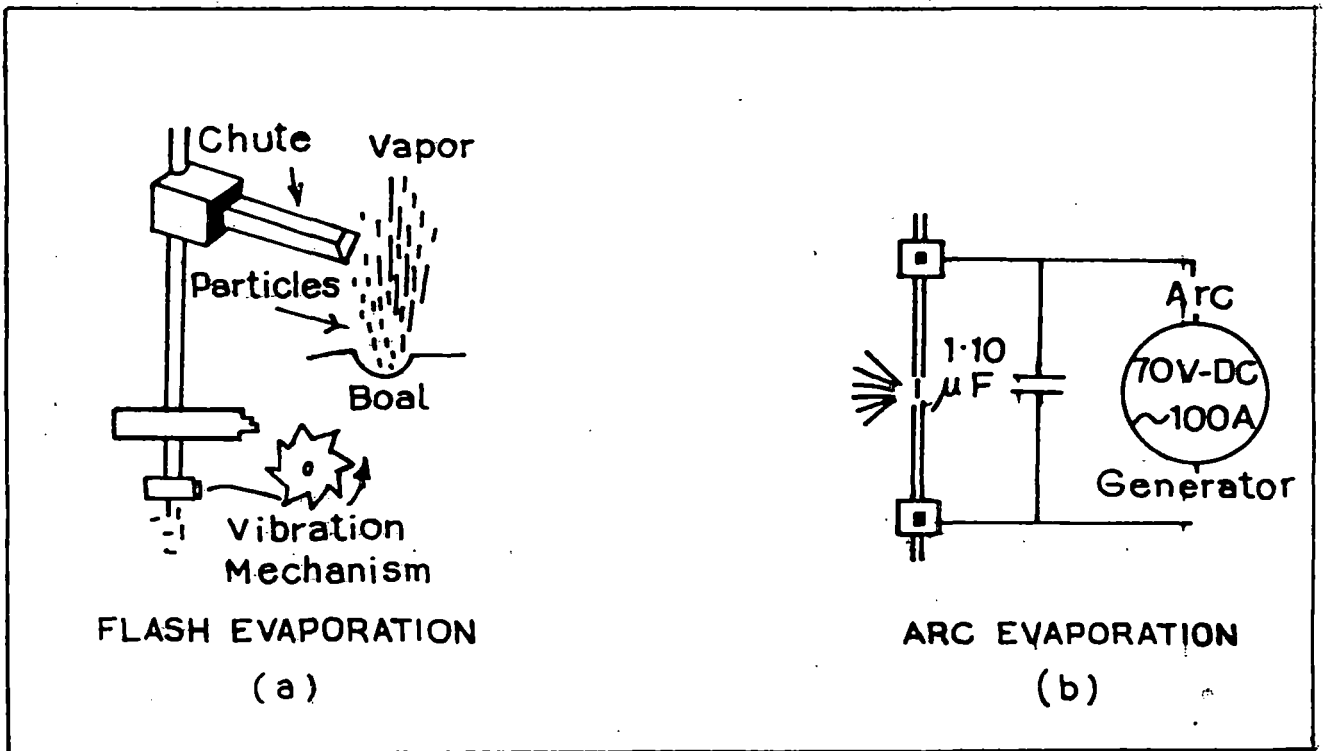


Figure 1.1. Schematic diagram of different evaporation technique

(a) Flash evaporation, (b) Arc evaporation.

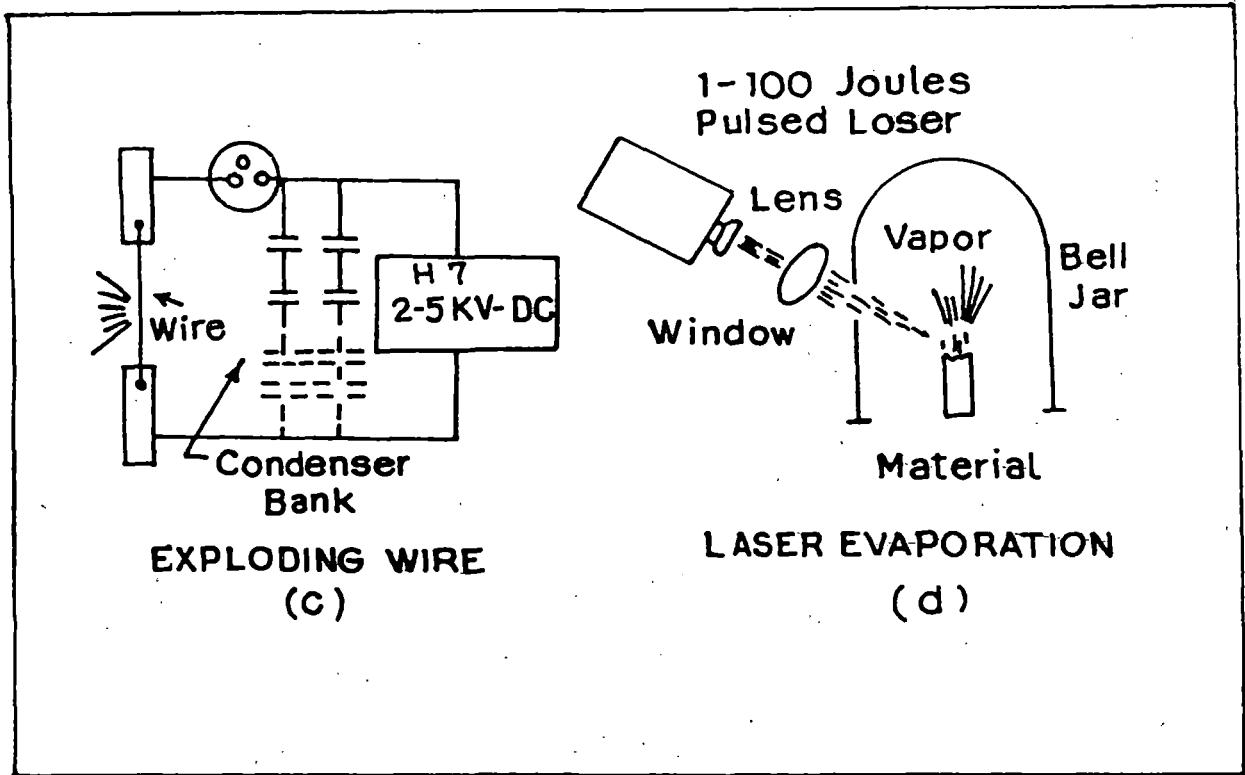


Figure 1.1. Schematic diagram of different evaporation technique
(c) Exploding-wire evaporation, (d) Laser evaporation.

1.2.2. Sputtering techniques: Vapour species may be created by kinetic ejection from the surface of a material (called the target) by bombardment with energetic and non-reactive ions. The ejection process, known as sputtering, takes place as a result of momentum transfer between the impinging ions and the atoms of the target surface. The sputtered atoms are condensed on a substrate to form a film. Various sputtering techniques are used for deposition of thin films.

Several systems have been employed for deposition of films by sputtering. These sputtering variants are shown schematically in figure 1.2. The simplest and most widely used one utilizes the glow discharge between two electrodes and is commonly referred to as a diode arrangement [Fig. 1.2.(a)]. The substrate in such a diode system is normally placed on the anode and kept at anode potential. It will acquire a negative potential of several volts relative to the anode and attracts gas ions, leading to contamination of the film. On the other hand, if the substrate is held at a large negative potential, the film will be subjected to steady ion bombardment throughout its growth. This technique [Fig. 1.2.(b)] employed by Maissel and Schaible [9], is called "bias sputtering". The idea of sputter deposition with simultaneous sputter cleaning by bombardment was originally conceived by Frerichs [10], and his arrangement is shown in figure 1.2.(c). Here an asymmetric alternating rather than d.c. is applied between cathode and substrate so that more material is deposited on one half-cycle than is removed by reverse sputtering in the other half-cycle. Bombardment removes absorbed gases and is responsible for good bonding of the film.

The effect of sputter-cleaning of an evaporated film is utilized in a system [Fig. 1.2.(d)] called "ion plating" [11]. The films are obtained by evaporation from a filament and the deposit is simultaneously bombarded with accelerated gas ions.

The efficient gettering action of films for reactive gases during deposition was put to advantage by Theuerer and Hauser [12] in the technique [Fig. 1.2.(e)], called "getter sputtering". In this case, two cathodes of the material to be sputtered are

symmetrically located with respect to a Ni anode cylindrical can. The first cathode is used to maximize the gettering action of active gases where they enter near the bottom of the cylindrical can. After sputtering for a few minutes, the sputtered materials from the second cathode is allowed to deposit on the substrate.

Auxiliary electrons may be supplied thermionically from a filament. Both the total ionization and the ionization efficiency are increased by accelerating the electrons by means of a third electrode and injecting them into the plasma. This sputtering [Fig.1.2 (f)] process, is called "triode sputtering".

Ionization of the gas can be produced by suitable electromagnetic radiations such as rf, uv, x-rays, and γ -rays. High ionization yield may be obtained conveniently by the use of rf of several megacycles (RF sputtering). The rf may be applied directly to the anode through a capacitor [Fig.1.2.(g.1.) for metal sputtering], or via a high-frequency coil inside [Fig.1.2.(g.2.)] or outside the discharge vessel. Gawehn [13] used the electrodeless technique with rf of 1.8 to 12 Mc/sec to sputter at low pressure. Note that rf may be used additionally in any one of the Fig 1.2.(a) to 1.2.(f) sputtering arrangements to obtained increased sputtering rates at lower pressures.

Davidse and Maissel [14] described the application of the rf technique to sputtering of insulator films. A transmitter or a standerd rf heating power suply (1 to 20 Mc/sec, 2 kW at 2 kV) may be used to couple directly to the insulator target mounted on a metal plate. Two cathodes in a push-pull arrangement may be used [Fig. 1.2.(g.3)]. The direct coupling of rf is somewhat sensitive to the design of the feed through for the insulator cathode and to the rf power input. The reflective losses from the power supply into the sputtering apparatus necessitate water cooling of the leads. For supporting and stabilizing the high-frequency discharge, a magnetic field is frequently applied. It also makes operation possible at low pressures of a few milli-torr. Very pure films can be obtained by this technique because chances of contamination are less at the low pressure involved. Quartz and various glasses may be readily deposited to form films at rates of up

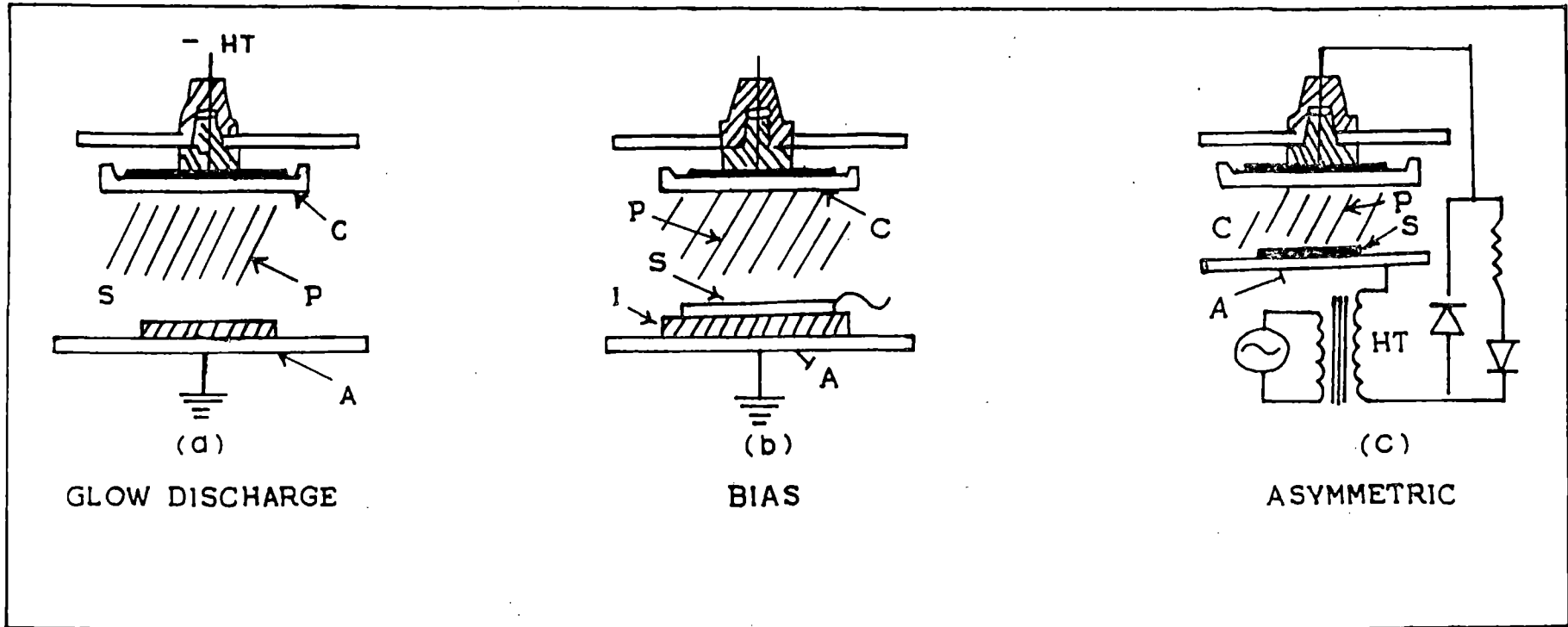


Figure 1.2. Schematic arrangement for several sputtering variants:

(a) Diode sputtering; (b) dc bias; (c) ac asymmetric (or bias);

The notations are P, plasma or discharge; C, cathode; A, anode; S, substrate; LT, lowtension; HT high tension.

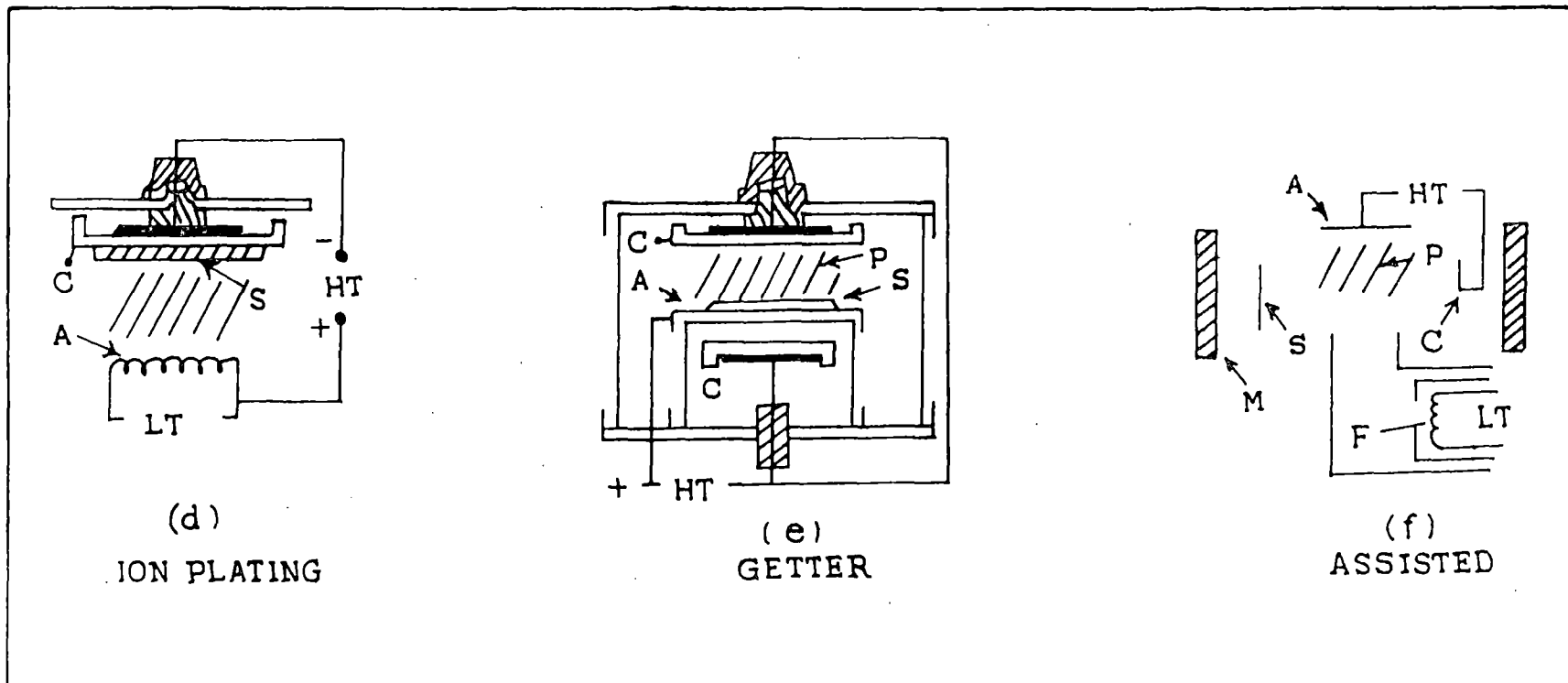


Figure 1.2. Schematic arrangement for several sputtering variants:

(d) ion plating; (e) getter sputtering; (f) thermionically and/or magnetically assisted glow discharge;

The notations are P, plasma or discharge; C, cathode; A, anode; S, substrate; LT, lowtension; HT high tension; M, magnet; F, filament (electron source);

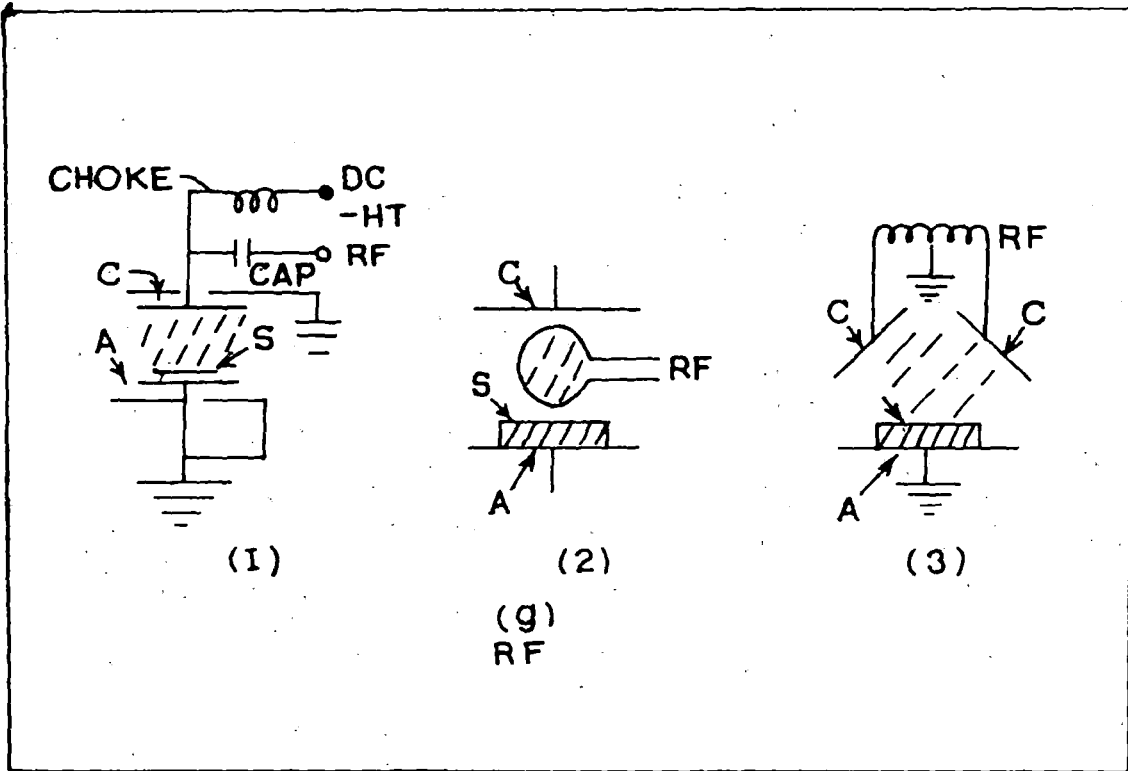


Figure 1.2. Schematic arrangement for several sputtering variants:

(g) rf sputtering with (1) capacitor coupling for sputtering of metals and the inductor coupling for isolating dc from rf power supply, (2) indirect or induced rf coupling and (3) push-pull double cathode;

to 30 Å/sec. under typical operating conditions of a 13.56 Mc/sec, rf power of 800 W at 3,000 V peak to peak and an axial magnetic field of 0.011 T.

These processes are best suited for depositing films of many type of multicomponent materials.

1.3. EPITAXIAL DEPOSITION

Both for the case of single component and multicomponent compounds, it is possible to monitor and control the kinetics of condensation and thermodynamic reactions of the various ad-atoms so that the deposition takes place literally monolayer-by-monolayer on a single-crystal substrate and the atomic arrangement in the film follows that in the single-crystal. It has been used primarily for basic single-crystal growth studies and for specialized micro-electronic applications. Hot Wall Epitaxy (HWE), Molecular Beam Epitaxy (MBE) and Grapho-epitaxy are commonly known. MBE is a sophisticated and expensive method. For this method ultra-high-vacuum (UHV) is required to provide a clean ambient. With the help of MBE technique it is possible to deposit epitaxial layers of compound semiconductors, such as $Zn_xCd_{1-x}S$ [15], GaAs and CdTe having precisely controlled properties. A schematic diagram of an MBE system is shown in figure 3.

In the above, very brief accounts of the important Physical Vapour Deposition (PVD) techniques have been given. The deposition processes which are related to our techniques belong to the chemical methods of deposition. So in the next section the chemical methods of deposition are discussed in more detail. More elaborate accounts are available in the standard text books [2 & 16-20].

Chemical methods may be classified in two categories:

- (i) Chemical vapour deposition and
- (ii) Solution deposition technique.

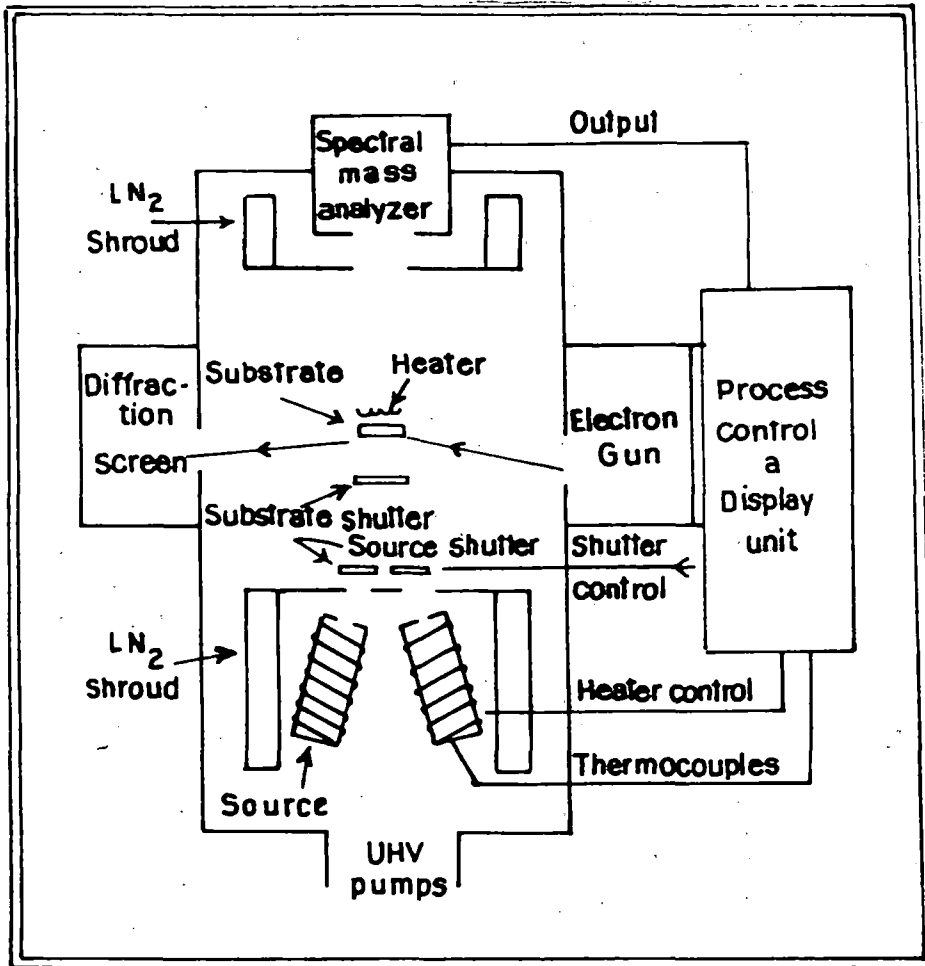


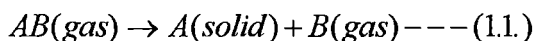
Figure 1.3. Schematic diagram for an MBE system.

1.4. CHEMICAL VAPOUR DEPOSITION

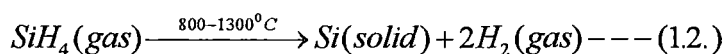
When a volatile compound of the substance to be deposited is vaporised, and the vapour is thermally decomposed or reacted with other gases, vapours, or liquids at the substrate to yield non-volatile reaction products which deposit atomistically (atom by atom) on the substrate, the process is called Chemical Vapour Deposition [21, 22]. Since a large variety of chemical reactions are available, CVD is a versatile and flexible technique in producing deposits of pure metals, semiconductors and insulators.

The chemical reactions utilized in CVD processes can be classified as: (i) decomposition reactions, (ii) reduction reactions, (iii) chemical transport reactions, etc.

1.4.1. Thermal decomposition:- Some compounds (such as organometallics, halides or metal hydrides) decompose at a high temperature on the substrate to yield metallic or semiconductor films. A general decomposition reaction can be written as



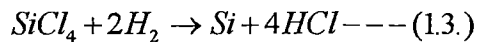
A typical example of the decomposition process activated by heat (pyrolytic decomposition) is



Most organo-metallic compounds decompose at relatively low temperatures ($< 600^\circ\text{C}$) and metal halides, particularly the iodides, are decomposed at higher temperatures. It is more convenient to use organo-metallic compounds as the processing can be carried out at lower temperatures. For example, thin films of Al_2O_3 can be prepared by thermal decomposition of aluminium tri-ethoxide at 550°C and aluminium tri-isopropoxide at 420°C .

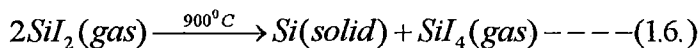
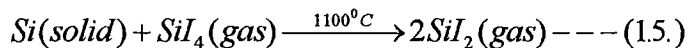
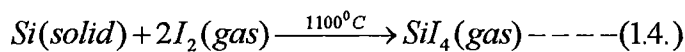
1.4.2. Reduction:- A reduction reaction may be considered as a decomposition reaction aided by the presence of another vapour species, called the reductant. A reduction reaction occurs at temperatures much lower than the unaided decomposition reaction.

A typical example of CVD by reduction is the preparation of Si from the corresponding halide vapours using H_2 or Zn as the reducing agent, according to the reaction



The use of H_2 , which is not a very strong reductant, offers the advantage that it can be premixed with the halide vapours without causing a premature reaction in the gaseous phase which gives rise to powdery deposits.

1.4.3. Chemical Transport: - The term chemical transport refers to the process of transferring of a nonvolatile deposit material to the substrate with the help of a highly volatile chemical vapour which converts it to a volatile compound by a chemical reaction. The volatile compound, formed as a consequence of this reaction, then decomposes on the substrate to yield a film of the source material. A typical example is the transport of Si in I_2 vapours.



Among the important materials which can be deposited by CVD techniques are semiconductors such as II - VI and III - V compounds, Si, and conducting doped oxides of Sn, In, and V, insulators such as SiO_2 , Si_3N_4 , BN, Al_2O_3 , Ta_2O_5 , TiO_2 , Nb_2O_5 , and AlN, and a number of metals [23 - 27].

The commonly used CVD systems cover a wide range from extremely simple laboratory setups to highly sophisticated, completely automated, electronically controlled and computerized industrial reactors. The systems can be either closed, permitting complete recovery of the reagent species and recycling, or open, requiring an external supply of source material and extraction of the reaction components. A typical CVD system used for the deposition of Si p-n junction structures is shown in Fig.1.4.

1.4.4. Major advantages of the CVD technique

(i) In general, low-vacuum facilities are required and, thus a relatively simple setup and fast recycling are possible; (ii) high ($\sim 1 \mu\text{m} / \text{min.}$) deposition rates are possible; (iii) it is possible to deposit compounds with easily controlled stoichiometry; (iv) it is relatively easy to dope the deposit with controlled amounts of impurities; (v) it is possible to deposit multicomponent alloys; (vi) refractory materials can be deposited at relatively lower temperatures as compared to vacuum evaporation; (vii) epitaxial layers of high perfection and low impurity content can be easily grown; (viii) objects of complex shapes and geometries can be coated; and (ix) in situ chemical vapour etching of the substrates prior to deposition is possible.

1.4.5. Drawbacks of the CVD technique

(i) The generally complex thermodynamics and reaction kinetics are poorly understood; (ii) comparatively higher substrate temperatures are required than those in the corresponding Physical Vapour Deposition (PVD) techniques ; (iii) the reactive gases used for deposition and the volatile reaction products formed are, in most cases, highly toxic, explosive, or corrosive; (iv) the corrosive vapours may attack the substrate, the deposited film, and the materials of the deposition setup; (v) the volatile

products generated during the deposition process may lead to incorporation of impurities in the film; (vi) the high substrate temperatures may lead to diffusion, alloying or chemical reaction on the substrate surface, thus restricting the choice of the substrate; (vii) high substrate temperatures may also give rise to segregation effects when metastable multicomponent materials are being deposited; (viii) masking of the substrate is generally difficult.

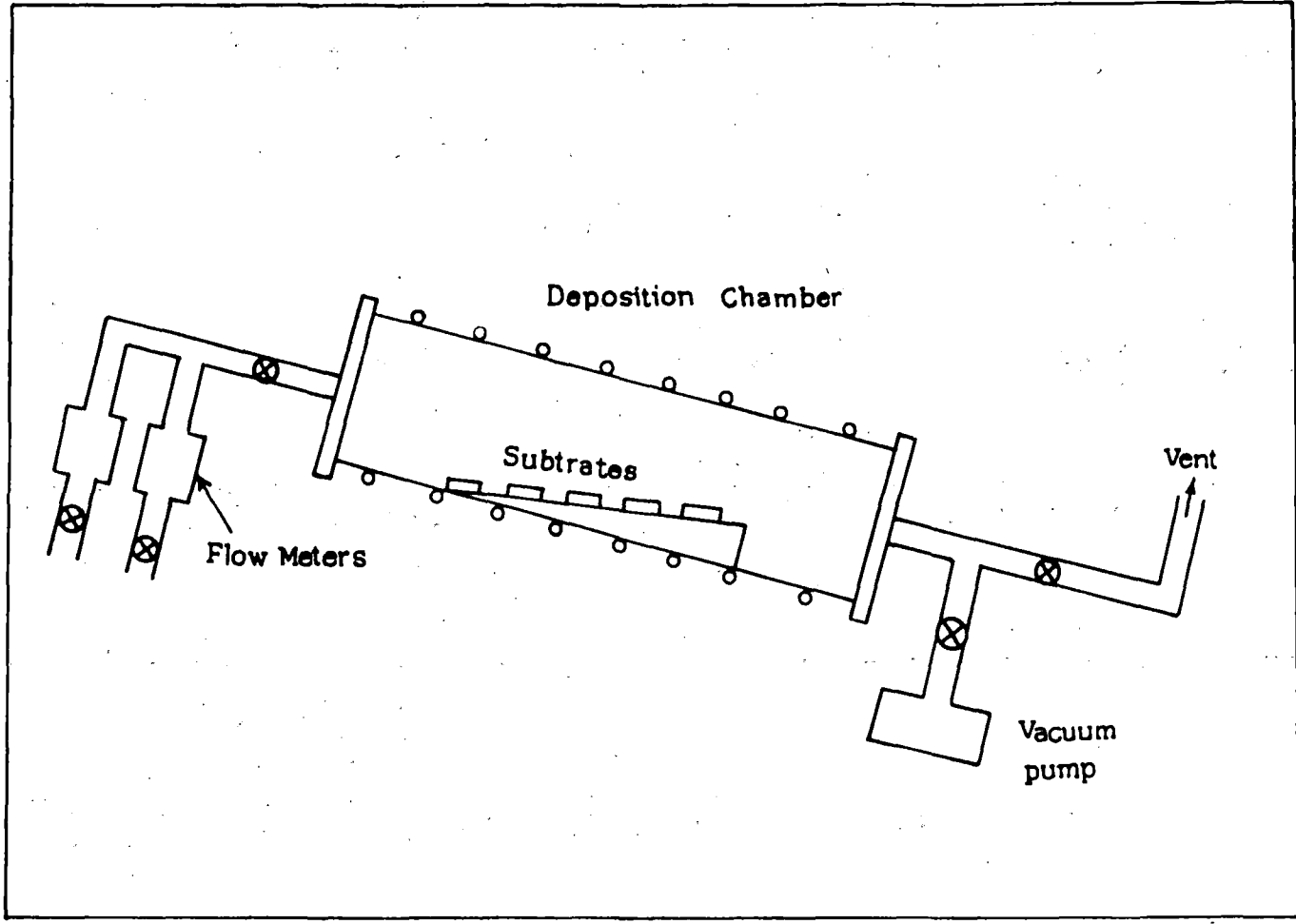


Figure 1.4. A typical chemical vapour deposition system.

1.5. Solution Deposition Techniques

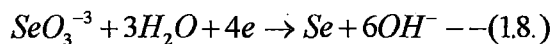
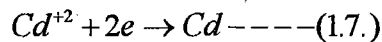
In these techniques, the material to be deposited are dispersed in a liquid medium (generally aqueous) and are always present in ionic form. Solution deposition techniques, therefore, inherently involve chemical and / or electrochemical reactions for the formation of the deposit material. The solution deposition techniques may be classified into two categories: (i) electrochemical deposition (ECD) and (ii) chemical solution deposition (ESD).

1.5.1. Electrochemical Deposition (ECD)

Electrochemical deposition techniques require an external source of current for deposition. Obviously, they also require electrically conducting substrates. Various ECD techniques are used for deposition of films, and electrodeposition is one of them.

1.5.1.1. Electrodeposition:- The occurrence of chemical changes due to the passage of electric current through an electrolyte (salt solution or molten salt) is termed electrolysis, and the deposition of any substance on an electrode as a consequence of electrolysis is called electrodeposition. The main constituent of the electrolyte which serves to provide ions either in their simple form or in complex form. Additional chemicals such as wetting agents, brightening agents, alkalis, and acids may be added with the electrolyte as required. Almost all metals (except for highly electronegative ones) can be electrodeposited from aqueous solutions. Alloys can be deposited by coelectrolysis, for which the electrode potentials should be brought very close to each other. Electrodeposition of compound semiconductors like CdSe, CdTe, Ag₂Se and GaAs is possible by co-depositing the two components in elemental form by cathodic reduction of their corresponding ions and their subsequent reaction to form

the corresponding compound. For example, deposition of CdTe film involves electrolytic codeposition of Cd and Te from Cd^{+2} and TeO_3^{-2} ions. Similarly, CdSe and GaAs are electroeposited from Cd^{+3} and SeO_3^{-2} ions and Ga^{+3} and AsO_2^{-2} ions, respectively. The reaction involved at the cathode, for example, in the case of CdSe, are



A schematic block diagram of the experimental setup for electrodeposition technique is shown in figure 1.5. Using this technique semiconducting metal chalcogenides such as CdS, HgS, PbS, Ti_2S , Bi_2S , Cu_2S , NiS, CoS and SnS/SnS_2 thin film can be deposited on various substrates.

1.5.1.2. Anodization:- When a current is passed through an electrolyte, an anode (metal substrate) is converted to one of its compounds. This conversion process is called anodization. The chemical composition of the film depends on the type of electrolyte. Acidic or basic electrolytes lead to oxide films, whereas thiourea and ammonia in the anodizing solution produce sulphide and nitride films respectively.

1.5.1.3. Cathodic conversion:- This is an electroconversion process for the deposition of Cu_2S films on CdS. In this method, $CuSO_4$ taken as an electrolyte, CdS thin film is used as a cathode and a copper plate as an anode. On passing a current Cu_2S films can be deposited on CdS film according to the following reaction.



In this reaction Cd^{+2} , goes into the solution.

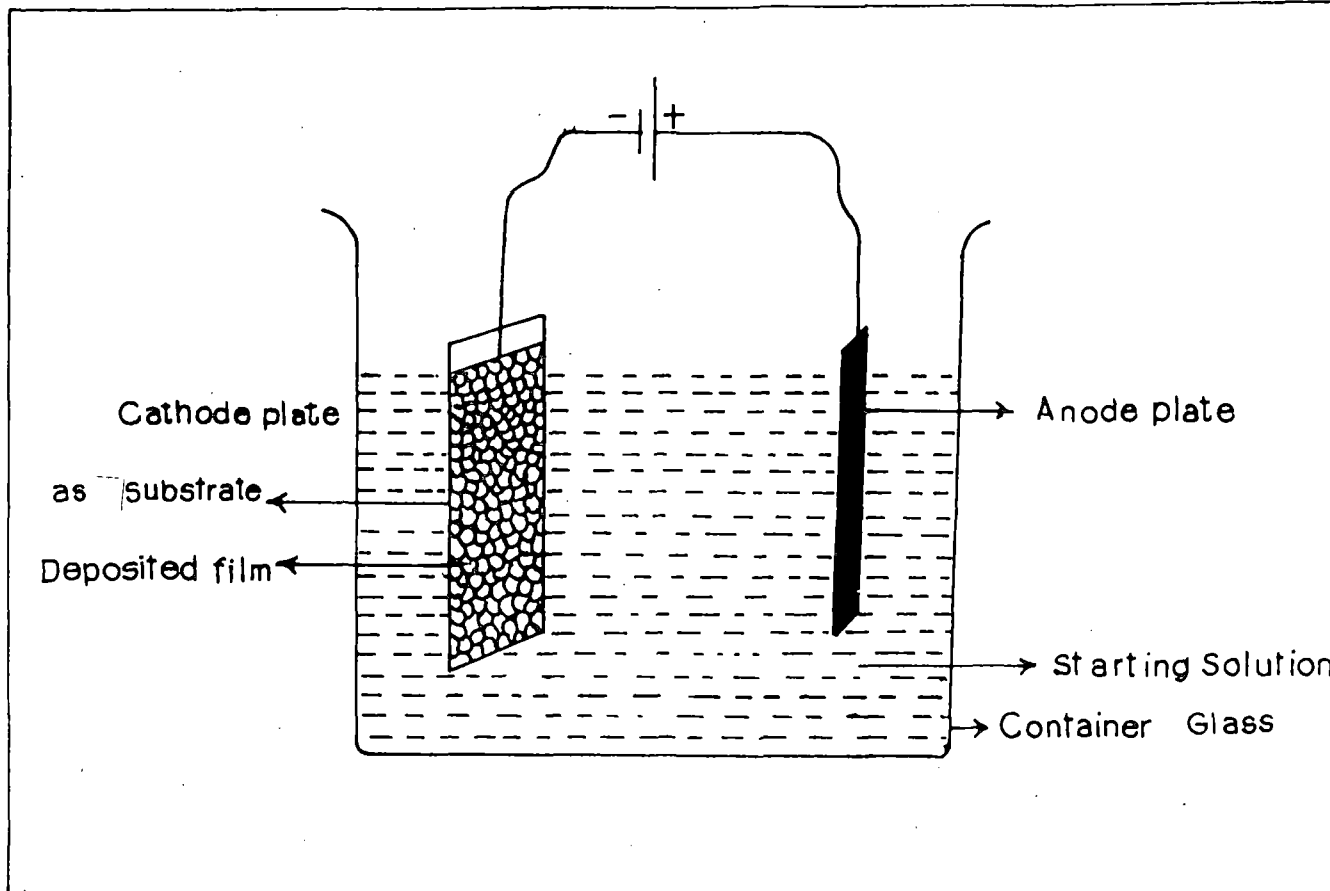


Figure 1.5. Schematic diagram of electrodeposition technique.

1.5.2. Chemical Solution Deposition (CSD)

Chemical solution deposition techniques are generally immersion technique in the sense that they involve simply dipping of the substrate into the reaction mixture for some time depending of the thickness required. Spray Pyrolysis, Solution Growth and Sol-gel techniques are the most popular among Chemical Solution Deposition techniques. The main advantages of these techniques are:-

(i) uniform deposition takes place, (ii) Both conducting and insulating substrates can be coated and (iii) No power supply is required. The various CSD techniques are:

1.5.2.1. Spray Pyrolysis:- A large number of metallic salt solutions when sprayed onto a hot substrate decompose to yield oxide films. Similarly films of sulfides or selenides can be prepared by pyrolytic decomposition of a solid complex compound formed on the surface of a substrate by spraying a mixed solution of the corresponding metallic salt and a sulphur / selenium-bearing compound. For example, CdCl_2 and $(\text{NH}_2)_2\text{CS}$ (thiourea) solutions when mixed at room temperature do not react to form CdS , but when sprayed onto a substrate held at $\sim 400^\circ\text{C}$, a solid complex of composition $\text{CdCl}_2 \cdot (\text{NH}_2)_2\text{CS}$ is formed, which decomposes on the substrate to yield CdS films.

A schematic block diagram of a typical spray-pyrolysis setup for deposition of metallic oxide, metallic sulfide and metallic selenide thin films is shown in figure 1.6. The atomization of the chemical solution into a spray of fine droplet is effected by the spray nozzle with the help of a filtered carrier gas which may or may not be involved in the pyrolytic reaction. For example, oxygen (O_2) is used as a carrier gas for the deposition of SnO_x film whereas the carrier gas plays no role in the deposition of CdS films. The carrier gas and the solution are fed into the spray nozzle at pre-

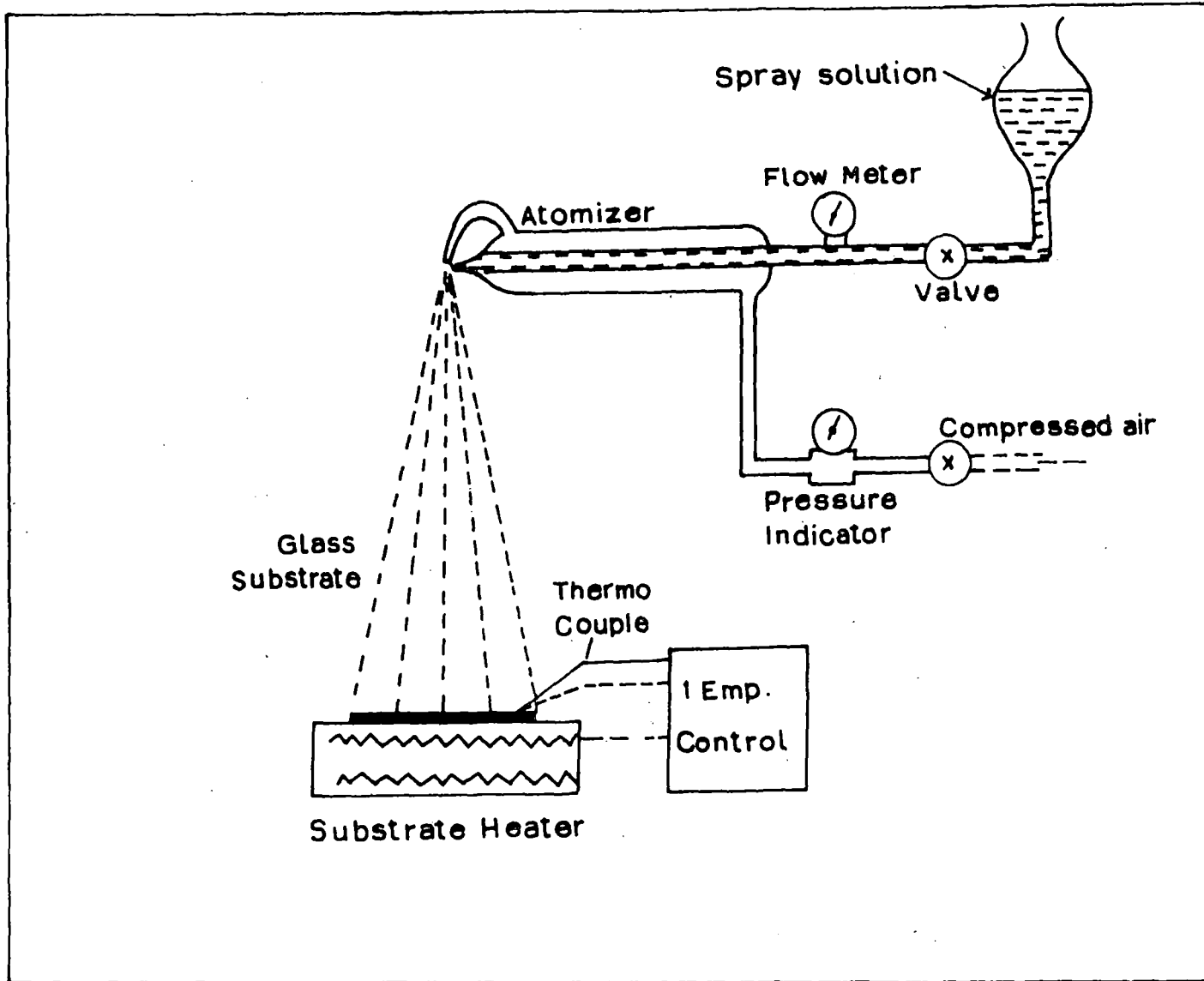


Figure 1.6. Schematic diagram of spray pyrolysis setup.

determined and constant pressure and flow rates. The substrate temperature is maintained with the help of a feedback circuit.

By this method doped and mixed films can be prepared very easily, simply by adding to the spray solution a soluble salt of the desired dopant or impurity. Two very important examples of the materials deposited by this technique [23 - 38] for device fabrication are (i) CdS for solar cells and (ii) In F-or Sb-doped SnO₂ for conducting glass.

1.5.2.2. Chemical Solution Growth:- The chemical solution growth technique, well known for chalcogenide films, has been extended to the deposition of oxide films (MnO₂, Fe₂O₃, ZnO and SnO₂). Metal ions in aqueous solution, under certain conditions, form solid phases of hydroxides M(OH)_n or hydrous oxides (M₂O.X H₂O) which on heating yield the corresponding metal oxides. With the help of controlled homogeneous precipitation from solution, S and Se compound films like CdS, PbS, ZnS, Bi₂S₃, CdSe, PbSe, ZnSe etc. have been successfully deposited by this technique [39, 40]. The major parameters which control the deposition process are the composition of the deposition bath, its pH and its temperature. The experimental setup to obtain film deposition is shown schematically in fig 1.7. The substrates are immersed vertically in the reaction bath, which is stirred continuously with a magnetic stirrer. The temperature of the bath is monitored by a contract thermometer that forms a part of a feedback circuit controlling the heater to maintain a constant temperature. When ionic product (IP) of the metal and chalcogenide ions exceeds the solubility product (SP) of the corresponding chalcogenide, a metal chalcogenide film is formed on the substrate by an ion-by-ion condensation process.

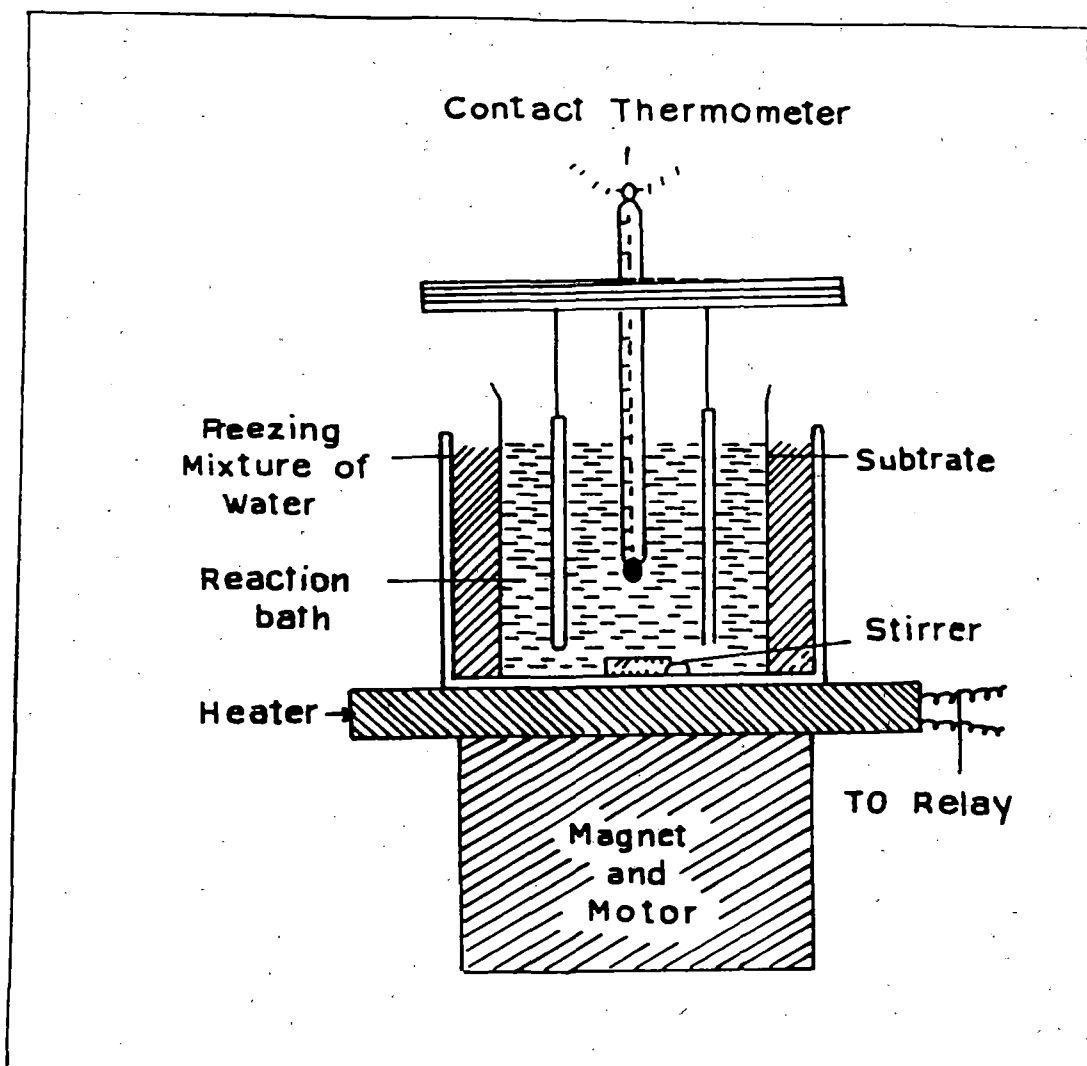
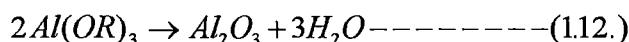
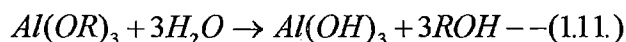


Figure 1.7. Experimental arrangement for solution growth setup.

1.5.2.3. Sol-Gel Method:- In this method for the preparation of thin films, a homogeneous solution is first prepared using metal alkoxides. The solution changes to a sol and then to a gel at room temperature. This gel forms thin gel-sheets which are converted to a glassy layer on heating to a high temperature. For instance, thin SiO₂ layers can be obtained from silicon tetra-ethoxysilane Si(OC₂H₅)₄ at a temperature of 500° C - 900° C. The films presents the possibility of obtaining thin glass sheets of thickness ranging from several tens to several hundreds of micrometers. With the help of this method one can also prepare bulk glasses and glass fibres. Fibres like silica-alumina or pure silica can be prepared by heating after drawing from alkoxide solution at near room temperature.

1.5.2.4. Dip Technique:- The dip technique [41-43] consists essentially of inserting the substrate into a solution containing hydrolysable metal compounds and pulling it out at a constant speed in atmospheric condition, when a liquid layer adheres to the substrate surface. It is then baked at high temperature, when a chemical reaction takes place producing the desired thin films. Any hydrolysable compound including halides or nitrates, preferably metallo-organics are suitable for this process. A typical reaction in the case of metal alkoxides is



The important control parameters are the viscosity of the solution, the pulling speed and the firing temperature. The rate of heating also needs to be controlled to avoid cracking of the films.

This technique has not been very popular, because so far it was limited to oxide films only. But as described in detail in chapter 2, it can be used to deposit sulphide thin films also.

1.5.3. Major advantages of Solution Deposition Techniques

(i) Experimental setups are much less sophisticated compared to those in vapour deposition techniques; (ii) no expensive equipment such as vacuum systems is not required for the deposition; and (iii) deposition is carried out at much lower temperatures ($< 100^{\circ}\text{C}$).

1.5.4. Drawbacks of Solution Deposition Techniques

Solution deposition techniques suffer from the drawback that preparation of ultraclean substrates using in situ techniques, such as plasma etching and ion bombardment as in the case of vapour deposition techniques, is not possible. Also the choice of the substrate is limited to only water-insoluble materials.

1.6. MISCELLANEOUS METHODS

1.6.1. Electrophoretic deposition

In this process, electrically charged particles suspended in a liquid are deposited on an electrode by applying an electric field. Using this method, mainly metal alloys, compounds, polymers and mixture of various components can be deposited.

1.6.2. Screen printing

Schematic representation of the screen printing process is shown in figure 1.8. It involves positioning the substrate on a carriage, which is then brought beneath the screen so that the substrate is in accurate registration with the pattern on the screen. The pattern on the screen is photolithographically defined so that open mesh areas in the screen correspond to the configuration to be printed. The substrate, when in the printing position, is placed a short distance beneath the screen. A small amount of the paste is dispensed onto the upper surface of the screen. A flexible wiper, called the squeegee, then moves across the screen surface, deflecting the screen vertically and bringing it into contact with the substrate and forcing the paste through the open mesh areas. On removal of the squeegee, the screen regains its original position by its natural tension, leaving behind the printed paste pattern on the substrate. The substrate carriage is then removed from beneath the screen and the substrate replaced and the process continues.

1.6.3. Spin coating

Spin coating differs from dip - coating in that the deposition film thins by centrifugal draining and evaporation. Bornside et al. [44] divide spin - coating into four stages: deposition, spin - up, spin - off and evaporation. An excess of liquid is dispensed on the surface during the deposition stage. In the spin - up stage, the liquid flows radially outward, driven by centrifugal force. In the spin - off stage ,

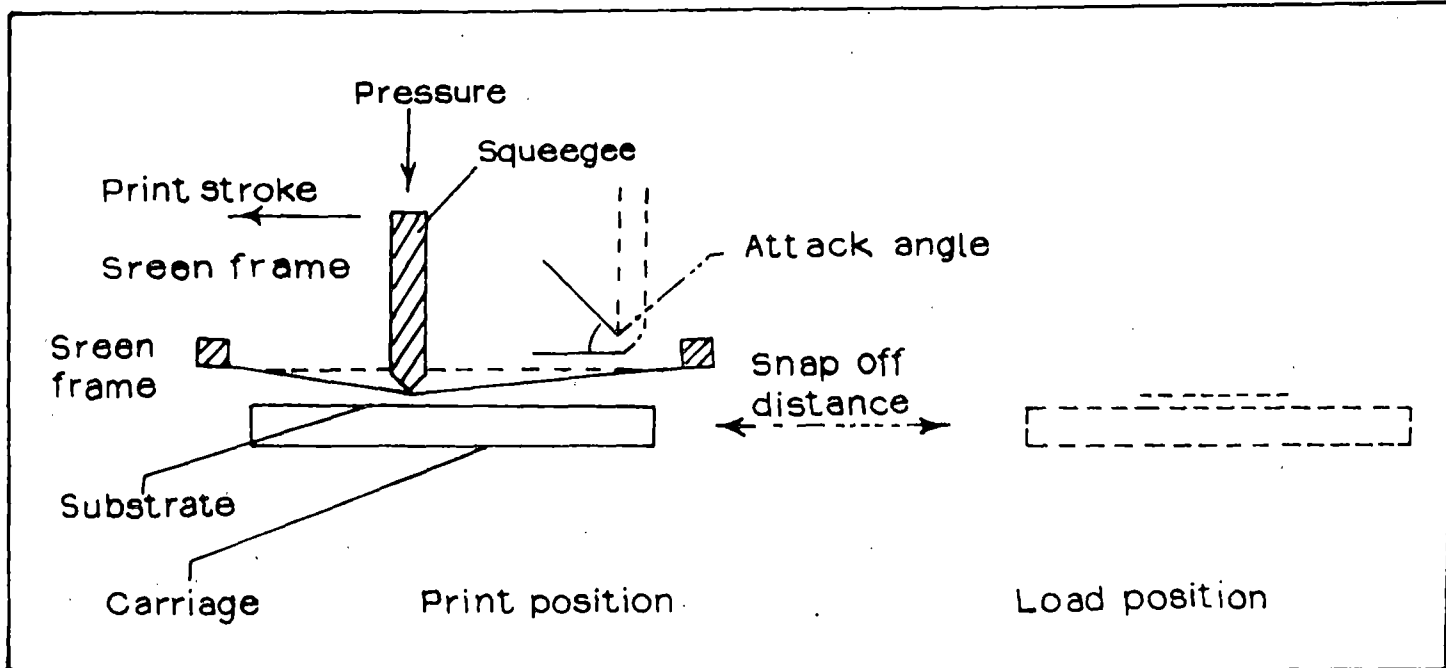


Figure 1.8. Schematic diagram of the screen printing process.

excess liquid flows to the perimeter and leaves as droplets. As the film thins, the rate of removal of excess liquid by spin - off slows down, because the thinner the film, the greater resistance to flow, and because the concentration of the non - volatile components increases, raising the viscosity. In the final stage, evaporation takes over as the primary mechanism of thinning. According to Scriven [45] the main advantage of spin - coating is that a film of liquid tends to become uniform in thickness during spin - off and, once uniform, tends to remain so, provided that the viscosity is not shear - dependent and does not vary over the substrate.

1.6.4. Solution Casting

In this method the solution is poured a horizontally placed substrate and leaving it for the solvent to evaporate. And then very thick ($\sim 100\mu\text{m}$) films can be formed on the substrate. The dried film can be stripped off the substrate very easily.

1.7. CONCLUSIONS

A large variety of methods for depositing thin solid films at rates ranging from a fraction of an angstrom to $10^6 \text{ \AA}/\text{sec}$ have been successfully utilized by various workers. Several of these methods, notably thermal evaporation and sputtering, permit automatic monitoring and controlling of the rate of deposition and hence film thickness. The fact that the properties of the films depend on various deposition parameters should be considered in the choice of a particular deposition technique. The parameters are the rate of deposition, temperature or kinetic energy of the vapour atoms, angle of incidence of vapour, electrostatic charges carried by vapours, the substrate temperature and vapour-source materials, concentration of the solution, composition of the ambient atmosphere, and thermal accommodation and condensation coefficients of the vapour atoms and the ambient gas atoms. These parameters may vary from technique to technique.

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