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Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction (SILAR) method

H M PATHAN and C D LOKHANDE*
Department of Physics, Shivaji University, Kolhapur 416 004, India

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Abstract. **During last three decades, successive ionic layer adsorption and reaction (SILAR) method, has emerged as one of the solution methods to deposit a variety of compound materials in thin film form. The SILAR method is inexpensive, simple and convenient for large area deposition. A variety of substrates such as insulators, semiconductors, metals and temperature sensitive substrates (like polyester) can be used since the deposition is carried out at or near to room temperature. As a low temperature process, it also avoids oxidation and corrosion of the substrate. The prime requisite for obtaining good quality thin film is the optimization of preparative provisos viz. concentration of the precursors, nature of complexing agent, pH of the precursor solutions and adsorption, reaction and rinsing time durations etc.**

In the present review article, we have described in detail, successive ionic layer adsorption and reaction (SILAR) method of metal chalcogenide thin films. An extensive survey of thin film materials prepared during past years is made to demonstrate the versatility of SILAR method. Their preparative parameters and structural, optical, electrical properties etc are described. Theoretical background necessary for the SILAR method is also discussed.

Keywords. **Metal chalcogenides; thin solid films; SILAR method.**

1. Introduction

Any solid or liquid system possesses at most two-dimensional order of periodicity called ‘thin film’. Properties of thin film often differ significantly from those of bulk due to surface and interface effects, which may dominate the overall behaviour of these films. Thin films are of particular interest for fabrication of large area arrays, solar selective coatings, solar cells, photoconductors, sensors, antireflection coatings, interference items, polarizers, narrow band filters, IR detectors, wave guide coatings, temperature control of satellites, photothermal solar coatings etc. Thin films can be fabricated in various ways. The techniques can be divided into physical and chemical methods. In physical methods, the film material is moved from a target source with some form of energy to the substrate. This method is widely used in one-compound films, like metal films. Under physical methods we have vacuum evaporation and sputtering, where the deposition has been transferred to gaseous state either by evaporation or an impact process. Chemical film fabrication method involves chemical reaction and the precursors are mostly components undergoing reaction at the substrate surface or in the vicinity of the substrate. Under chemical methods we have the gas phase chemical processes such as conventional chemical vapour deposition (CVD), laser CVD, metal organochemical deposition (MOCVD) and plasma enhanced chemical vapour deposition. Liquid phase chemical techniques include electrodeposition, chemical bath deposition, electroless deposition, anodization, spray pyrolysis etc.

One of the newest solution methods for the deposition of thin film is successive ionic layer adsorption and reaction (SILAR) method, which is also known as modified version of chemical bath deposition. In spite of its simplicity, SILAR has a number of advantages: (i) it offers extremely easy way to dope film with virtually any element in any proportion by merely adding it in some form of the cationic solution, (ii) unlike closed vapour deposition method, SILAR does not require high quality target and/or substrates nor does it require vacuum at any stage, which is a great advantage if the method will be used for industrial application, (iii) the deposition rate and the thickness of the film can be easily controlled over a wide range by changing the deposition cycles, (iv) operating at room temperature can produce films on less robust materials, (v) unlike high power methods such as radio frequency magnetron sputtering (RFMS), it does not cause local over heating that can be detrimental for materials to be deposited and (vi) there are virtually no restrictions on substrate material, dimensions or its surface profile. Moreover, it is relatively inexpensive, simple and convenient for large area deposition. It can be carried out in

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*Author for correspondence

glass beakers. The starting materials are commonly available and cheap materials. As it is a chemical method, a large number of varieties of substrates can be coated. Thus, any insoluble surface to which the solution has free access will be a suitable substrate for the deposition. The deposition is carried out at or close to room temperature, avoids oxidation or corrosion of metallic substrates. Stoichiometric deposit is easily obtained. Since the basic building blocks are ions instead of atoms, the preparative parameters are easily controllable and better orientation and improved grain structure can be obtained.

In chemical bath deposition (CBD) method, deposition of metal chalcogenide semiconducting thin films occurs due to substrate maintained in contact with dilute chemical bath containing metal and chalcogen ions. The film formation on substrate takes place when ionic product exceeds solubility product. However, this results into precipitate formation in the bulk of solution, which cannot be eliminated. This results in unnecessary formation of precipitation and loss of material. In order to avoid such unnecessary precipitation, a CBD is modified and known as successive ionic layer adsorption and reaction (SILAR) method. In this modification, thin films are obtained by immersing substrate into separately placed cationic and anionic precursors and rinsing between every immersion with ion-exchanged water. The rinsing time in ion exchange water is critical for ionic layer formation. Thus, precipitation formation i.e. wastage of material, is avoided in SILAR method.

The successive ionic layer adsorption and reaction (SILAR) method is relatively a new and less investigated method, first reported in 1985 by Ristov *et al*. The name SILAR was ascribed to this method by Nicolau (1985) and discussed in subsequent papers of Nicolau and coworkers (Nicolau and Minnard 1988; Nicolau *et al* 1988), which deals with ZnS, CdZnS and CdS thin films. The SILAR method is useful for the deposition of thin films of chalcogenide groups I–VI, II–VI, III–VI, V–VI, VIII–VI binary and I–III–VI, II–II–VI, II–III–VI, II–VI–VI and II–V–VI ternary chalcogenides and composite films.

2. Concept of solubility and ionic product

Sparingly soluble salt, AB, when placed in water, a saturated solution containing A^+ and B^- ions in contact with undissolved solid AB is obtained and an equilibrium is established between the solid phase and ions in the solution as

$$AB\,(S) \rightleftharpoons A^+ + B^-. \tag{1}$$

Applying the law of mass action,

$$K = [C_A^+ \cdot C_B^-]/C_{AB}, \tag{2}$$

where C_A^+, C_B^- and C_{AB} are concentrations of A^+, B^- and AB in the solution, respectively. The concentration of pure solid is a constant number, i.e.

$$C_{AB}\,(S) = \text{constant} = K', \tag{3}$$

$$K = [C_A^+ \cdot C_B^-]/K', \tag{4}$$

$$KK' = C_A^+ \cdot C_B^-. \tag{5}$$

Since K and K' are constants, the product of KK' is also constant, say K_s, therefore (5) becomes

$$K_s = C_A^+ \cdot C_B^-. \tag{6}$$

The constant, K_s, is called solubility product (SP) and $(C_A^+ \cdot C_B^-)$ is called the ionic product (IP). When the solution is saturated, the ionic product is equal to the solubility product. But when the ionic product exceeds the solubility product, i.e.

$$IP/SP = S > 1, \tag{7}$$

the solution is supersaturated (S = degree of supersaturation), precipitation occurs and ions combine on the substrate and in the solution to form nuclei. Temperature, solvent and particle size (Skoog and West 1963; Alexeyev 1971; Pietrzyk and Frank 1974; Lincot and Borges 1992) affect the solubility product. For any formation of thin film, there is some minimum number of ions or molecules, which produce a static phase in contact with solution, called nucleus. Nucleation on the substrate of surface starts at local homogeneity. The rate at which nuclei forms on the surface of the substrate, depends on the degree of supersaturation.

It is assumed that the formation of stable growth centres on the surface, $N(t)$, can be expressed as a function of total number of active sites on the surface, N_0, by the law

$$N\,(t) = N_0\,[1 - \exp\,(-At)], \tag{8}$$

where A is nucleation rate constant. From these stable growth centres, various models have been proposed to describe either bidimensional (monolayer) or three-dimensional growth (Lokhande 1991).

Growth of particles, already present in the solution takes place in second step, when nuclei or other seed particles are present. In case of ionic solids, the process involves deposition of cation and anion on appropriate sites.

$$(AB)_n + A^+ + B^- \rightarrow (AB)_{n+1}, \tag{9}$$

$$(AB)_{n+1} + A^+ + B^- \rightarrow (AB)_{n+2}, \tag{10}$$

where n is the minimum number of A^+ and B^- required for giving stable phase, $(AB)_n$. The growth rate is directly proportional to the supersaturation

$$\text{Rate of growth} = K_0' a(Q-S), \tag{11}$$

where a is surface area of the exposed solid and K_0' the constant which is a characteristics of the particular precipitate. If the supersaturation is maintained at low level throughout the precipitation, relatively few nuclei are formed. That will grow to give a small number of large particles with high supersaturation, many more nuclei are formed initially and nucleation may occur through the precipitation process. As a result, there are great number of centres upon which growth process can take place, none of the particles grow very large and colloidal suspension is formed. The colloidal suspension consists of finely divided solid particles in a liquid phase with diameter about 0·01–0·1 m. Under some circumstances, colloidal particles can come together and adhere to one another and the resulting solid is called colloidal precipitate and the process by which it is formed is called coagulation or agglomeration. Colloidal particles when agglomerated have quite different properties from a crystalline solid since the particles are arranged irregularly.

The growth kinetics of a thin film deposition process is of two types: (i) ion-by-ion growth where deposition process involves the ion-by-ion deposition at nucleation sites on the immersed surfaces and (ii) according to Lundin and Kitaev (1965), nucleation takes place by adsorption of the colloidal particles and growth takes place as a result of surface coagulation of these particles, giving thin and adherent film. This is known as cluster-by-cluster growth of the film.

3. Theoretical background of SILAR

The successive ionic layer adsorption and reaction (SILAR) method is mainly based on the adsorption and reaction of the ions from the solutions and rinsing between every immersion with deionized water to avoid homogeneous precipitation in the solution. The collection of a substance on the surface of another substance is known as adsorption, which is the fundamental building block of the SILAR method. The term adsorption can be defined as the interfacial layer between two phases of a system. Adsorption may be expected when two heterogeneous phases are brought into contact with each other. Hence, gas–solid, liquid–solid and gas–liquid are three possible adsorption systems. In SILAR method, we are only concerned with adsorption in liquid–solid system. Adsorption is an exothermic process. The adsorption is a surface phenomenon between ions and surface of substrate and is possible due to attraction force between ions in the solution and surface of the substrate. These forces may be cohesive forces or Van-der Waals forces or chemical attractive forces. Atoms or molecules of substrate surface are not surrounded by atoms or molecules of their kind on all sides. Therefore, they possess unbalanced or residual force and hold the substrate particles. Thus, adatoms can be holding on the surface of the substrate. The factors like temperature of solution, pressure, nature of the substrate, concentration of the solution, area of the substrate etc affect the adsorption process. The reaction in pre-adsorbed (cations) and newly adsorbed (anions) forms the thin films of desired material.

3.1 *Basic of SILAR*

The SILAR is based on sequential reaction at the substrate surface. Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. The SILAR process is intended to grow thin films of water insoluble ionic or ion covalent compounds of the type $\mathrm{K}p\mathrm{A}a$ by heterogeneous chemical reaction at the solid solution interface between adsorbed cations, $p\mathrm{K}_{\mathrm{a}}^{+}$ and anion, $a\mathrm{A}_{\mathrm{p}}^{-}$, following the reaction

$$(p\mathrm{K}_{aq}^{a+} + q\mathrm{X}_{aq}^{b-}) + (b'\mathrm{Y}_{aq}^{q'+} + a\mathrm{A}^{p-}) \rightarrow$$
$$\mathrm{K}p\mathrm{A}a_{\mathrm{S}} \downarrow + q\mathrm{X}_{aq}^{b-} + b'\mathrm{Y}_{aq}^{q'+}$$
$$\text{with } ap = bq = b'q', \tag{12}$$

where, K represents cation (Cd^{2+}, Zn^{2+}, Fe^{3+}, Cu^{+}, etc), p represents the number of cations, a represents the numerical value of charge on cation, X is a ion in cationic precursors having negative charge ($\mathrm{X} = \mathrm{SO}_4^{2-}$, Cl^{-}, NO^{3-} etc), q represents the number of X in cationic precursors and b the numerical value of charges on X, b' the number of Y in the anionic solutions, q' the numerical value of charge on Y, Y the ion which is attached to chalcogen ion, A represents the anion (O, S, Se and Te), a' the number of anions. A is the chalcogen ion. In the presence of complexing agent, above reaction can be written as

$$\mathrm{P}[(\mathrm{KC})^{a+}]_{aq} + q\mathrm{X}_{aq}^{b-} + b'\mathrm{Y}_{aq}^{q'+} + a\mathrm{A}^{p-} \rightarrow$$
$$\mathrm{K}p'\mathrm{A}a'_{\mathrm{S}} \downarrow + \mathrm{C} + q\mathrm{X}_{aq}^{b-} + b'\mathrm{Y}_{aq}^{q'+}, \tag{13}$$

where C is complexing agent. Figure 1 represents the basis of SILAR growth. It consists of atleast four different steps: adsorption, rinsing (I), reaction and rinsing (II).

Adsorption: In this first step of SILAR process, the cations present in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer. This layer is composed of two layers: the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative form the counter ions of the cations.

Rinsing (I): In this step, excess adsorbed ions, $p\mathrm{K}^{a+}$ and $a\mathrm{A}^{p-}$, are rinsed away from the diffusion layer. This results into saturated electrical double layer.

Reaction: In this reaction step, the anions from anionic precursor solution are introduced to the system. Due to the low stability of the material, $\mathrm{K}p\mathrm{A}a$, a solid substance is formed on the interface. This process involves the reaction of $p\mathrm{K}^{a+}$ surface species with the anionic precursor, $a\mathrm{A}^{p-}$.

Rinsing (*II*): In last step of a SILAR cycle, the excess and unreacted species aA^{p-}, X, Y, and the reaction byproduct from the diffusion layer are removed.

By repeating these cycles, a thin layer of material, K*p*A*a*, can be grown. Following the above-mentioned steps the maximum increase in film thickness per one reaction cycle is theoretically one monolayer. This results into a solid layer of the compound K*p*A*a*. Dividing the measured overall film thickness by number of reaction cycles, growth rate can be determined. This gives a numerical value for growth rate under the given conditions. If the measured growth rate exceeds the lattice constant of the material, a homogeneous precipitation in the solution could have taken place. In practice, however, the thickness increase is typically less than or greater than a monolayer. Thus, the process involves an alternate immersion of the substrate in a solution containing a soluble salt of the cation of the compound to be grown. The substrate supporting the growing film is rinsed in highly purified deionized water after each immersion.

The facts affecting the growth phenomena are the quality of the precursor solutions, their pH values, concentrations, counter ions, individual rinsing and dipping times. In addition, complexing agent and pretreatment of the substrate have been shown to affect the SILAR growth.

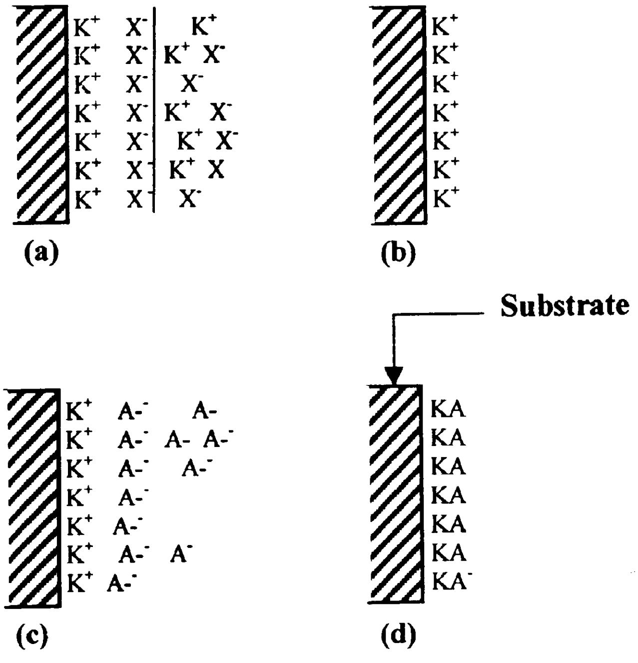

Figure 1. Schematic diagram of SILAR growth: (**a**) Adsorption of K^+X^- and the formation of electrical double layer, (**b**) rinsing (I) removes excess, unabsorbed K^+ and X^-, (**c**) reaction of A^- with pre-adsorbed K^+ ions to form KA and (**d**) rinsing (II) to remove excess and unreacted species and form the solid solution KA on surface of the substrate.

3.2 *Mechanism of SILAR method*

The growth mechanism involves three most important steps: (i) specific adsorption of the most strongly adsorbed ions of the compound to be grown, by the substrate immersion in a solution of one of its cationic precursor, (ii) water rinsing of the excess solution still adhering to the substrate, and (iii) chemical reaction between the most strongly specific adsorbed cations and the less strongly adsorbed anions by the subsequent substrate immersion in the solution.

In the following, in view of a better understanding but without limiting the generality of the process, we shall discuss the growth mechanism taking as an example the growth of CdS thin films. Solution of $CdSO_4$ and Na_2S are used as immersion baths. Figure 2 shows experimental set-up of manually operated SILAR deposition system. It mainly consists of beakers of cationic precursor ($CdSO_4$), anionic precursor (Na_2S) and highly purified water. For the deposition of binary chalcogenide (CdS) thin film, atleast four beakers are needed. The beakers of precursor and beaker of rinsing are alternately placed, each rinsing beaker being placed between a beaker containing a solution of a salt of the cation and another containing a solution of salt of the anion. For the deposition of CdS thin films, a well cleaned glass substrate is immersed in cationic precursor solution of $CdSO_4$ (figure 2a) in which Cd^{2+} and SO_4^{2-} ions are adsorbed on the surface of the substrate ($CdOH^+$ adsorption is neglected). The substrate is rinsed in ion exchange water (figure 2b) to remove unadsorbed Cd^{2+} and SO_4^{2-} ions. In order to avoid the homogeneous precipitation in the diffusion layer at the next immersion in the Na_2S solution, the rinsing time must be experimentally determined or calculated so that the residual activity of the Cd^{2+} in the diffusion layer $[Cd_r^{2+}]$ should be $[Cd_r^{2+}] < K_{so}[H^+]/K[HS^-]$. Here $K_{so} \cong 10^{-28}$ is the solubility product of CdS. The substrate is then immersed in an anionic precursor (figure 2c) solution. During the next immersion in the Na_2S solution, the HS^-, S^{2-}, OH^- and Na^+ ions diffuse from the solution in the diffusion layer towards solid solution interface until their concentration in the diffusion equals those in bath. The immersion time is experimentally calculated. The HS^- and S^{2-} enter the outer Helmoltz layer, react with the adsorbed Cd^{2+} and form CdS monolayer. This is followed by rinsing again in ion exchange water (figure 2d) to remove Cd^{2+}, S^{2-} ions, unreacted and loosely bounded CdS material and other byproducts. This completes one deposition cycle for the deposition of CdS film. By repeating such deposition cycles, continuous CdS films on the substrate surface is possible. The overall reaction can be written as

$$Cd^{2+}_{aq} + SO_4^{2-}{}_{aq} + 2Na^{+}_{aq} + S^{2-}_{aq} \rightarrow CdS\downarrow + 2\,Na^{+}_{aq} + SO_4^{2-}{}_{aq}. \qquad (14)$$

4. SILAR deposition systems

The critical operations for the deposition of thin films by successive ionic layer adsorption and reaction (SILAR) method, are adsorption of the cations, rinsing with deionized water, reaction of pre-adsorbed cations with newly adsorbed anions and again rinsing with deionized water. Generally, manual, electropneumatic and computer based systems have been used to perform these operations in SILAR method. These methods are discussed in brief in the following sections.

4.1 *Manually operated*

This system does not require any power supply for operations, hence it is economical. In this system, four or more glass beakers of typically 50 ml capacity containing precursor solutions and deionized water are placed separately in the tray. The beakers containing precursor solutions and deionized water are alternately placed as shown in figure 2. The beaker containing deionized water is placed in between the beakers containing cationic and anionic precursor solutions. The immersion and rinsing of substrates are done manually. The SILAR deposition of sufficiently thick film requires many hours and therefore manual deposition of certain materials is not possible for a single person.

4.2 *Computer based*

The schematic diagram of computer-based operating system (Nicolau 1985; Jim’enez-Gonz’ailez and Nair 1995) is shown in figure 3. The equipment consists of two beakers of 50 ml each containing the precursor solution and two rinsing vessels, lying in a circle on the circular tray. Each rinsing vessel being placed in between beakers containing cationic and anionic precursor solutions. The substrates are attached vertically by means of four arms. The arms are set out in line or a right angle and supported on the spindle. The spindle can turn and slide tightly in a bearing. Two steeping motors drive it. The computer program governs the vertical and translation movement of the spindle.

4.3 *Microprocessor based*

The schematic diagram of microprocessor-based operating system is shown in figure 4. The equipment is feasible for elemental, binary, ternary, composite etc materials.

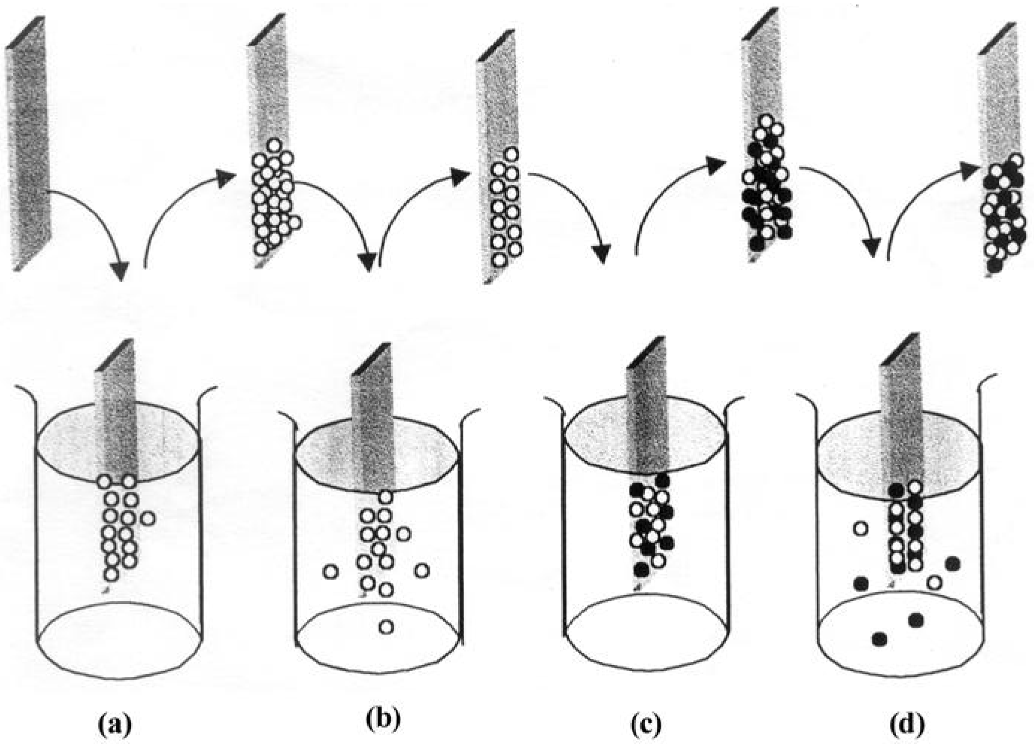

Figure 2. The scheme of SILAR method for the deposition of CdS thin films (○, Cd^{2+}; ●, S^{2-}): (**a**) → cationic precursor, (**b**) → ion exchange water, (**c**) → anionic precursor and (**d**) → ion exchange water.

Each rinsing vessel being placed in between beakers containing cationic and anionic precursor solutions. The substrates are attached vertically by means of robotic arms. The microprocessor governs the vertical and translational movement of the robotic arms.

5. Metal chalcogenide films by SILAR method

Metal chalcogenide thin films prepared by SILAR method are of particular interest as in recent years, thin film technology has developed enormously due to the fact that one dimension of film is negligible and that is relatively easy to produce by SILAR method. The technology of thin films deals with the films of thickness between tenths of nanometers and several micrometers can be easily prepared by SILAR. The SILAR plays a pivotal role in the deposition of materials. This method is suitable for industrial application to develop synthetic materials of tailored properties for communication, information and solar energy conversion with decreased size of active electronic components, a higher packing density, higher seed performance and lower cost.

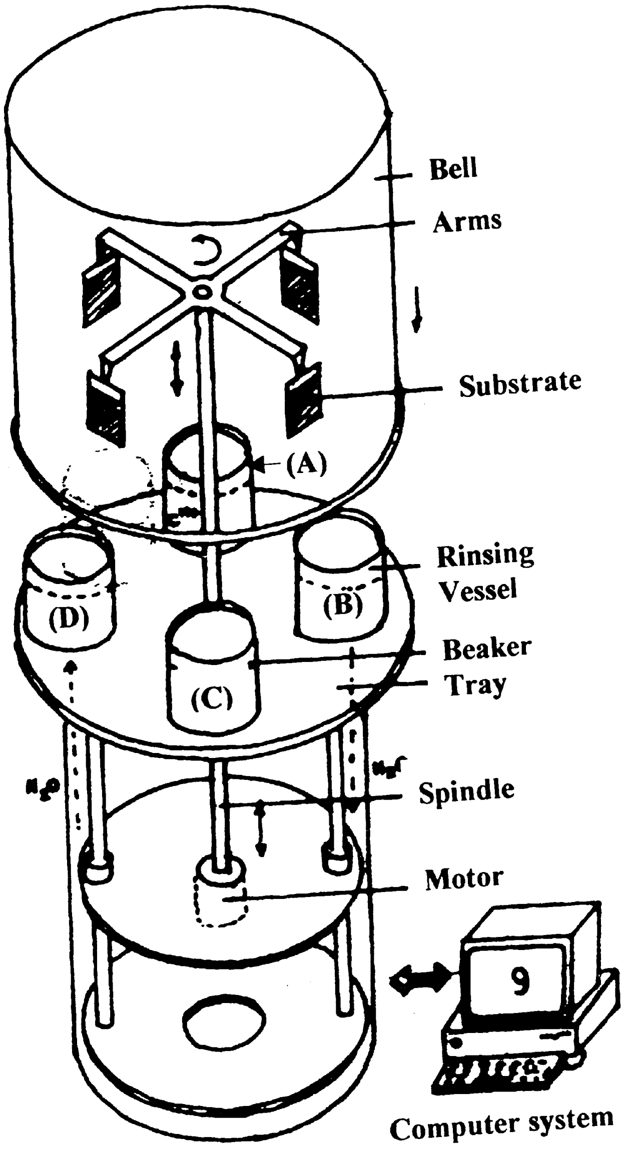

Figure 3. Computer based SILAR deposition system: (**a**) → cationic precursor, (**b**) → ion exchange water, (**c**) → anionic precursor and (**d**) → ion exchange water.

5.1 *Metal sulphide thin films*

5.1a *Copper sulphide*: Copper sulphide belongs to I–VI compound semiconductor material. At room temperature, copper sulphide (CuS) forms five stable phases: covellite (CuS), anilite ($Cu_{1\cdot7}S$), digenite ($Cu_{1\cdot8}S$), djurteite ($Cu_{1\cdot95}S$) and chalcocite (Cu_2S). Copper sulphide has different crystal structures depending upon the value of X such as hexagonal, orthorhombic, pseudo cubic and tetragonal. Cu_xS has hexagonal crystal structure and Cu_2S may be present in both the crystal structures viz. orthorhombic and hexagonal. Generally the films are blue-black in colour. The optical band gap of Cu_xS varies in the region of 1·2–2·5 eV. The variation in electrical conductivity is from 0·07 Ω^{-1} cm to 2400 Ω^{-1} cm as x varied from 2 to 1·8. It is a p-type semiconducting material. Copper sulphide thin films have received particular attention since the discovery of the CdS/Cu_xS heterojunction solar cell in 1954. Cu_xS thin films have been found to possess near ideal solar control characteristics: transmittance in the infrared region, low reflectance < 10% in the visible region so as to avoid glare and relatively high reflectance > 15% in the near infrared region. The films can also be used in laminated glazing. Cu_xS thin films have an interesting range of applications as photothermal conversion, electrocon-

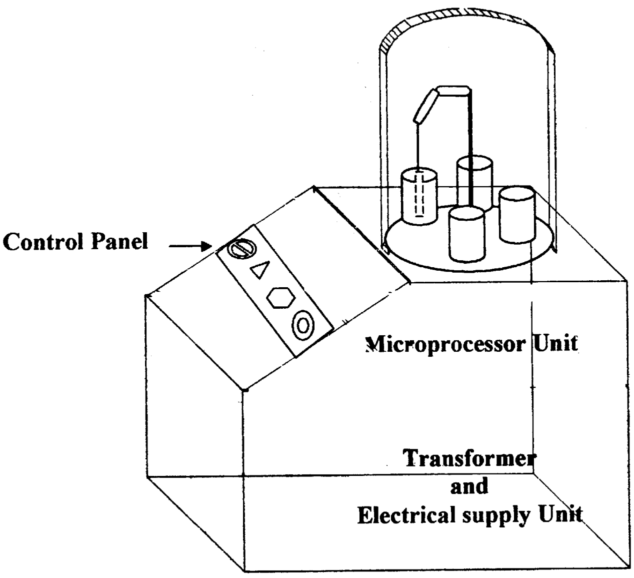

Figure 4. Microprocessor based SILAR deposition system.

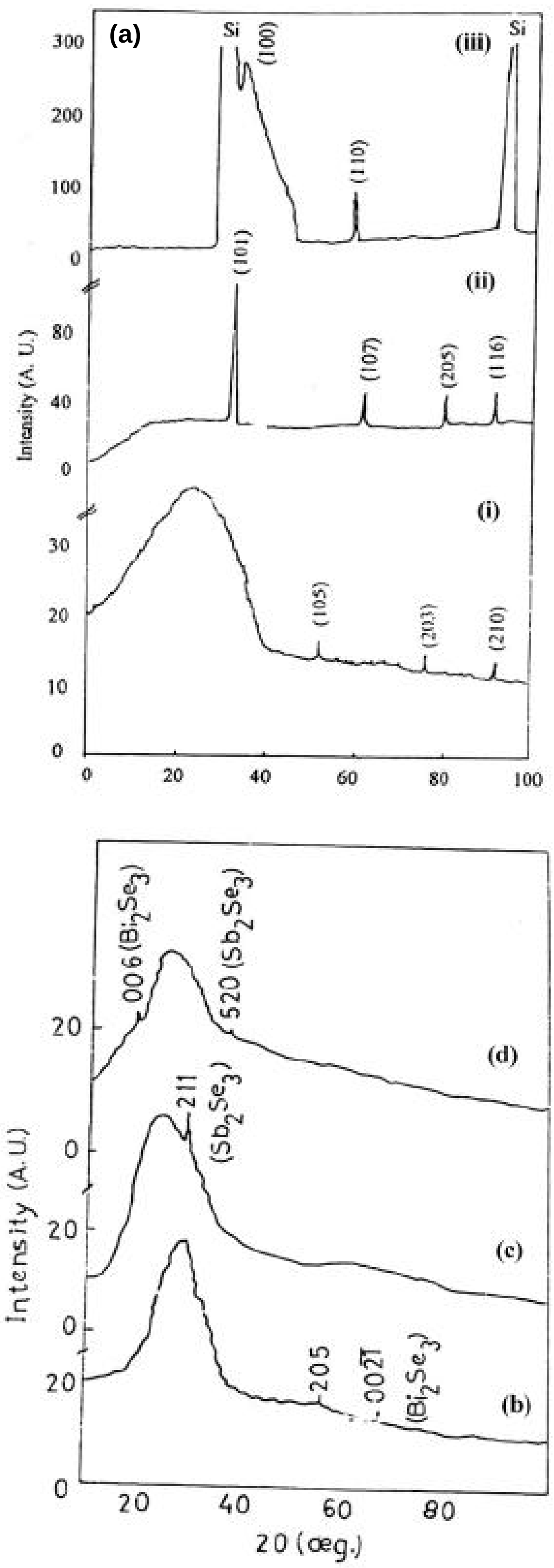

Figure 5. Typical X-ray diffraction patterns of SILAR deposited (**a**) MoS_2 thin films onto various substrates (i) amorphous glass, (ii) FTO coated glass and (iii) Si (111) wafer, (**b**) Bi_2Se_3, (**c**) Sb_2Se_3, and (**d**) Bi_2Se_3–Sb_2Se_3 thin films.

ductive electrode, microwave shielding and solar control coatings (Grozdanov and Najdoski 1995; Suarez and Nair 1996; Nascu *et al* 1997). It is also used in photo-detectors and in photovoltaic applications. The deposition of Cu_xS thin films, using SILAR method has been investigated by many workers (Lindroos *et al* 2000; Sartale and Lokhande 2000a; Pathan and Lokhande 2001a). Scanning electron micrograph of copper sulphide is shown in figure 6(e). The films are dense, smooth and homogeneous without visible pores. Figure 8(c) shows high-resolution transmission electron micrograph (HRTEM) of Cu_2S film. It shows that the film is composed of grains with diameter of about 8 nm, which confirms the nanocrystalline nature of Cu_2S films.

5.1b *Silver sulphide*: Silver sulphide belongs to I–VI compound semiconductor materials. It has monoclinic crystal structure. The optical band gap of Ag_2S is around 1·1 eV. The films are blackish. The electrical resistivity of the film was found to be of the order of $10^4\ \Omega$ cm. The Ag_2S shows *n*-type electrical conductivity. Thin films of Ag_2S have applications in photoconducting cells, IR detectors, solar selective coating, photovoltaic cell and photochemical cells.lb In the visible region and near IR region, Ag_2S barrier layer is used as detectors. Recently, the use of Ag_2S in the photoelectrochemical storage cells as a storage electrode has created much interest as the current efficiency of Ag/Ag_2S couple is about 90% (Hodes *et al* 1976; Lokhande and Pawar 1982). Sankapal *et al* (2001) reported the deposited Ag_2S thin films and photoelectrochemical (PEC) study was carried out by Pathan *et al* (2001a).

5.1c *Zinc sulphide*: Zinc sulphide belongs to II–VI compound semiconductor materials. ZnS thin films may be present in cubic or/and hexagonal crystal structure. Generally, the chemically deposited films are of mixed phases of cubic and hexagonal crystal structure. The optical band gap of ZnS thin films lies in between 3·6 to 4 eV. The electrical resistivity is of the order of $10^4\ \Omega\cdot$cm with *n*-type electrical conductivity. Zinc sulphide is an important semiconductor material with a large optical band gap (> 3·5 eV), which has vast potential use in thin film devices, such as photoluminescent and electroluminescent devices. Besides, ZnS could be an important material in short wavelength emitting diode. Fabrication of graded bandgap Cu(In, Ga)Se_2 thin film mini-modules with a (Zn, O, S, OH) buffer layer has been reported (Sushiya *et al* 1996). Many workers (Nicolau and Minnard 1988; Lindroos *et al* 1997, 1998; Lokhande *et al* 2002) investigated the deposition of ZnS. Manganese doped zinc sulphide (ZnS : Mn) thin films have been seen from their use in electroluminescent display. The deposition of ZnS : Mn thin film was carried out by Lindroos *et al* (1995). Figure 8 shows the high-resolution transmission electron micrograph (HRTEM) of $Zn_x(O, H)_y$ thin film. By HRTEM, random orientation of nanoparticles can be clearly seen. Small nanoparticles with dimensions (50–60 nm) are identified.

5.1d *Cadmium sulphide*: Cadmium sulphide belongs to II–VI compound semiconductor materials. Cadmium sulphide exists as a mixed phase (wuztite and zinc-blend). The optical band gap energy varies from 2·17 to 2·24 eV. The electrical resistivity of the CdS is of the order of 10^5 Ω·cm with *n*-type electrical conductivity and is often used in optoelectronic devices. Especially, in case of chalcopyrite heterojunction solar cells, it acts as a buffer layer. In the conventional absorber-window configuration of thin film heterojunction solar cells, *n*-CdS window have paired with *p*-Cu_2S, *p*-CdTe and *p*-$CuInSe_2$ absorber layers to result in efficient solar cells. Also, cadmium sulphide is a promising semiconducting material in the conversion of solar energy into electrical energy by means of PEC process. Cadmium sulphide (CdS) has been employed in high efficiency solar cells formed with Cu_2S (Hall and Meakin 1979), Cu(In,Ga)Se_2 (Dimmler and Schock 1996) and CdTe (Britt and Ferekides 1993). The CdS are also used as photoconductors, photo-resistors, and transistor image magnification and recently in light activated valves for large screen liquid crystal display. Many workers (Nicolau 1985; Nicolau and Minnard

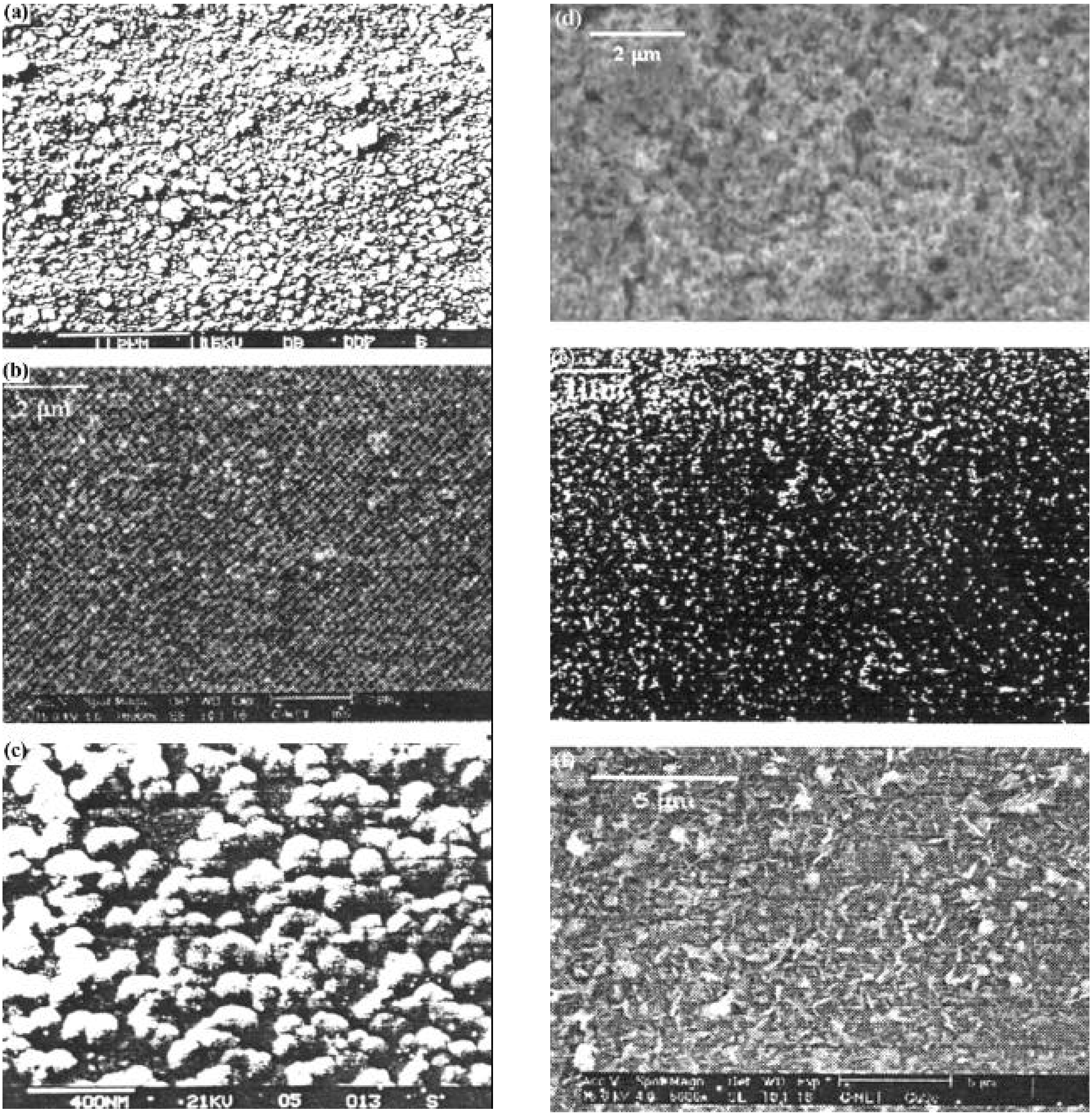

Figure 6. Typical SEMs of SILAR deposited (**a**) CdS, (**b**) InS, (**c**) Bi_2S_3, (**d**) InTe, (**e**) CuS and (**f**) CuSe thin films.

1988; Nicolau *et al* 1988; Valkonen *et al* 1997a,b; Sankapal *et al* 2000b; Lokhande *et al* 2001) have carried out the deposition of CdS. Scanning electron micrograph of CdS is shown in figure 6(a). The films are dense, smooth and homogeneous without visible pores. Figure 8(a) shows the high-resolution transmission electron micrograph (HRTEM) of CdS thin film. By HRTEM, random orientation of nanoparticles can be clearly seen. Plots of optical absorption against wavelength (inset) and $(ahn)^2$ against hn for SILAR deposited CdS thin film are shown in figure 9. Figure 10 shows the plot of log r against $(1000/T)$ CdS thin film. The room temperature electrical resistivity was found to be of the order of 10^6 Ω·cm.

Manganese doped cadmium sulphide (CdS : Mn) thin films are the potential candidates in thin film photovoltaic devices as window/buffer material. The basic requirement of buffer layer such as high resistivity, high band gap etc may be satisfied by CdS : Mn. The films of CdS : Mn was deposited by Kulkarni *et al* (2002).

5.1e *Indium sulphide*: Indium sulphide belongs to III–VI compound semiconductor materials. The InS has orthorhombic, In_2S_3 has tetragonal and In_6S_7 has monoclinic crystal structure. The band gap increases from 2·1 eV for pure In_2S_3 to 2·6 to 2·9 eV in the presence of oxygen. The films are dark greyish-red. The electrical resistivity is around the 10^7–10^9 Ωcm with *n*-type electrical conductivity. Depending upon temperature and pressure, it exists in different modifications (*a*, *b* and *g*). Its band gap varies between 2·0 and 2·9 eV, depending upon the composition and crystal size. The $Cu(In,Ga)Se_2$ based solar cell prepared with the chemically deposited In_2S_3 as a buffer layer reached the efficiency (15·7%) near to those obtained by device made with standard CdS buffer layer. The deposition of In_2S_3 by SILAR method is investigated by our group using $InCl_3$ and $In_2(SO_4)_3$ as a In source (Lokhande and Pathan 2000b; Pathan *et al* 2001b). Scanning electron micrograph of indium sulphide is shown in figure 6. The films are dense, smooth and homogeneous. Plot of log r against $(1000/T)$ for SILAR deposited indium sulphide thin film is shown in figure 10. The room temperature electrical resistivity is found to be of the order of 10^6 Ω cm.

5.1f *Tin sulphide*: Tin sulphide (SnS) belongs to IV–VI compound semiconductor materials. Tin sulphide appears to be in different phases as SnS, SnS_2 etc. The films are of brown colour. It has a band gap of 1·3 to 1·5 eV. The electrical resistivity is of the order of 10^4 –10^5 Ωcm with *p*-type electrical conductivity. The high conversion efficiency, ~ 25%, is obtainable in photovoltaic devices according to Prince–Loferski diagram and its acceptability from the point of view of cost, availability, toxicity and stability ascribe to SnS a unique position among the metal sulphides, probably to be shared only by FeS_2.

Tin disulphide (SnS_2) has hexagonal crystal structure. Tin disulphide is a layer compound with CdI_2 type structure, it is composed of a sheet of tin atoms sandwiched between two close packed sheets of sulphur atoms. The optical band gap energy is of the order of 2·6 eV. The electrical resistivity is of the order of 10^3 Ωcm with *n*-type electrical conductivity. Tin disulphide shows electrical and optical properties that are useful in many devices, such as current controlled devices, switching devices, and photoconducting cells (Patil and Fredgold 1971; Said and Lee 1973). The deposition of tin disulphide was carried out using SILAR method by Sankapal *et al* (2000c).

5.1g *Lead sulphide*: Lead sulphide belongs to IV–VI compound semiconductor materials. The colour of the film is greyish-black. Lead sulphide (PbS) has direct band gap of 0·4–0·78 eV. The electrical resistivity of the film is of the order of 10^5–10^6 Ωcm. Its absorption coefficient continuously increases from the infrared (150 cm^{-1} at 3 μm) through the visible region and has been used in infrared detectors since mid 1940s. The lead sulphide (PbS) is used in infrared sensors (Moss 1955; Slater 1956). In solar energy research, PbS thin films were investigated for photothermal conversion application either independently on metallic substrates (Gupta *et al* 1979; Agnihotri and Gupta 1981) or in stacked multilayer (Reddy *et al* 1981, 1987). The PbS films were deposited by Kanniainen *et al* (2000) and Resch *et al* (1997).

5.1h *Arsenic sulphide*: Arsenic sulphide belongs to V–VI compound semiconductor materials. It has monoclinic crystal structure. The optical bad gap energy is 2·38 eV. The electrical resistivity varies from 10^4–10^5 Ωcm with *n*-type electrical conductivity. Arsenic sulphide (As_2S_3) is a technically important class of material because of its good transparency in the 0·7–11 μm wavelength range and excellent resistance against moisture and corrosion. It is well known that As_2S_3 has a variety of applications in optical imaging, hologram recording, various electronic devices including electro-optic information storage devices and optical mass memories (Rawson 1967; Maruno *et al* 1971; Tanaka 1975; Tanaka and Ohtsuka 1979; Danko *et al* 1991). The deposition of arsenic sulphide was carried out by Sartale and Lokhande (2000b).

5.1i *Antimony sulphide*: Antimony trisulphide belongs to V–VI group materials. It has orthorhombic crystal structure. The density of Sb_2S_3 is 4·12 g/cm^3. The optical band gap of Sb_2S_3 is 1·8 eV. The electrical resistivity is around 10^4 Ωcm with *n*-type electrical conductivity. It finds some special application in the target material for television cameras, microwave devices, switching devices and various optoelectronic devices. It is also an important material in view of its photosensitive and thermoelectric properties. It has applications in paint and polymer industries, microwave devices, switching devices and various optoelectronic devices (Desai and Lokhande 1994). The Sb_2S_3 films were deposited by Sankapal *et al* (1999a). Figure 7 shows the 2D and 3D AFMs of Sb_2S_3 film. The film appears to be made up of fine particles or nanoparticles.

5·1j *Bismuth sulphide*: Bismuth sulphide belongs to V–VI compound semiconductor materials. Its occurring naturally in grey crystalline form is referred to as 'bismuth glance' or bismuthinite. Both natural and artificial crys-

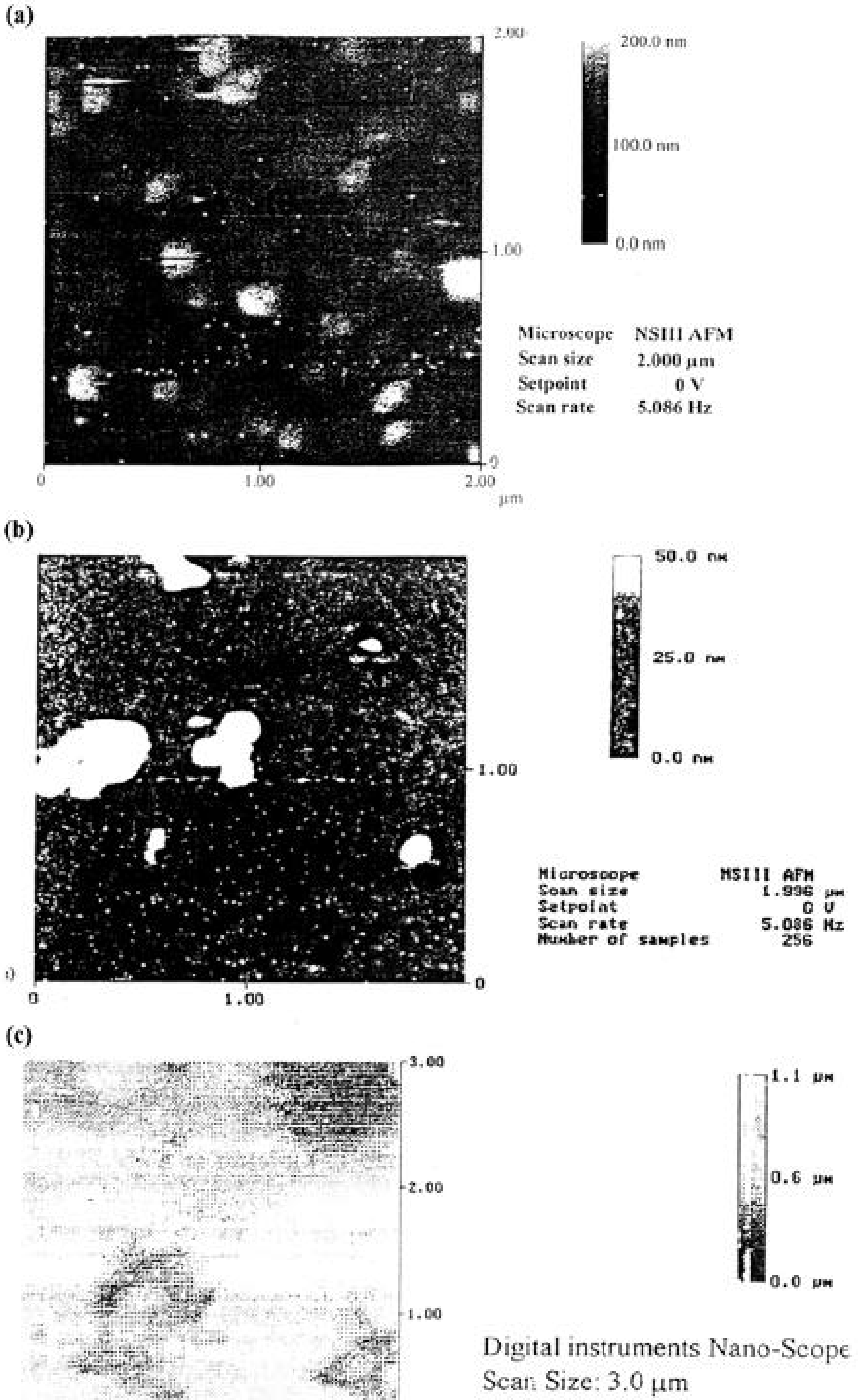

Figure 7. **a–c.**

talline forms belong to orthorhombic crystalline structure. Bi_2S_3 has orthorhombic crystal structure. Bi_2S_3 in thin film form is a promising semiconducting material for optoelectronic devices as its band gap energy lies in the range 1·2–1·7 eV (Peter 1979). The electrical resistivity of Bi_2S_3 is of the order of 10^4 Ω.cm. It is useful in the conversion of solar energy into electrical energy by means of PEC process (Miller and Heller 1976). It can also be used in heterojunction, IR detectors, Lux meters, switching devices, Schottky barrier etc. The films of Bi_2S_3 were deposited by Ahire *et al* (2001a, b). Scanning electron micrograph of Bi_2S_3 is shown in figure 6. The films are dense, smooth and of compact structure, consist of fine particles. Figure 7 shows the 2D and 3D AFMs Bi_2S_3 film. The film appears to be made up of fine particles or nanoparticles.

5.1k *Molybdenum disulfide* (MoS_2): Molybdenum disulphide belongs to VIb–VIa compound semiconductor materials. It has hexagonal crystal structure. Molybdenum disulfide exhibits layer type structure, in which monolayers of Mo are sandwiched between monolayers of sulphur, which are held together by relatively week Van der Waals forces. The optical and electronic properties of layered VI transition metal chalcogenide for efficient solar energy conversion, with low energy direct transition ($a = 10^5\ \text{cm}^{-1}$) at photon energy around 1·78 eV shows promise to convert solar energy in thin film structures. The electrical

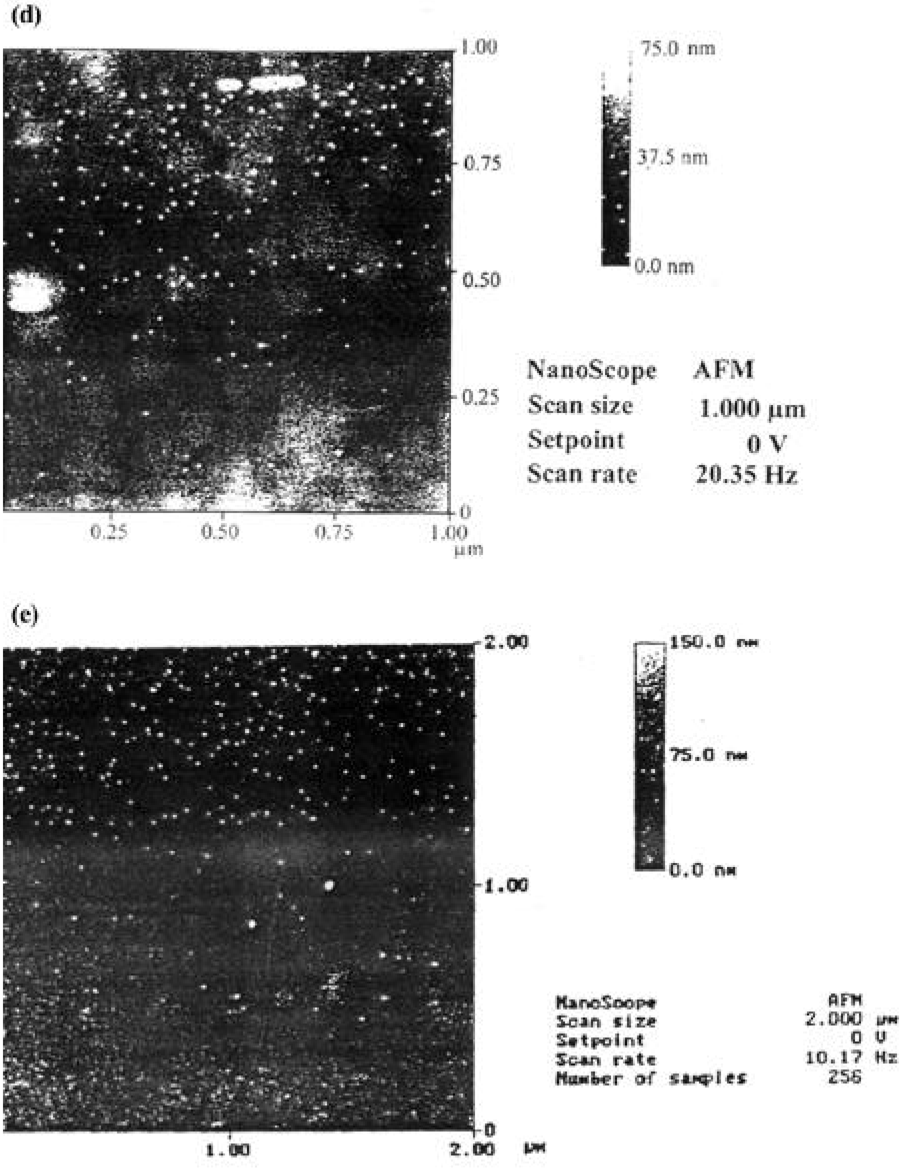

Figure 7. Typical AFMs of SILAR deposited (**a**) Bi_2S_3, (**b**) Sb_2S_3, (**c**) $CuInS_2$, (**d**) Bi_2Se_3 and (**e**) Sb_2Se_3 thin films.

resistivity of the MoS_2 film is of the order of 10^4 Ωcm. Molybdenum disulphide appears to be very promising semiconductor material for various applications such as solar cells, rechargeable batteries and solid lubricants for metallic and ceramic surfaces, high vacuum or high temperature applications. They have also been widely used in space technology where their low coefficient of friction in vacuum is of particular value. These applications exist from the optical, electrical and mechanical properties of this compound. The MoS_2 thin films were deposited by Sartale and Lokhande (2001a). X-ray diffraction patterns of MoS_2 films deposited onto amorphous glass, FTO coated glass and Si (111) wafer substrates are shown in figure 5A (i–iii). It was observed that films deposited onto amorphous glass substrate are nanocrystalline consisting of fine grains. However, films deposited onto FTO and Si substrates are microcrystalline.

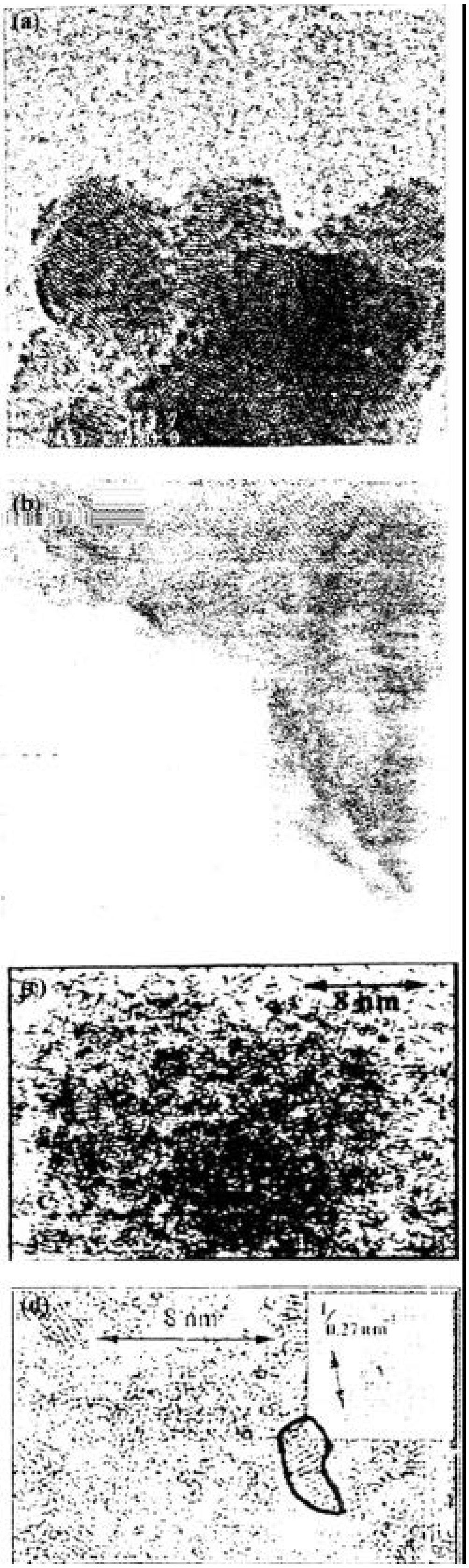

Figure 8. Typical HRTEMs of (**a**) CdS, (**b**) $Zn_x(O, S)_y$, (**c**) Cu_2S and (**d**) $CuInS_2$ thin films.

5.1l *Manganese sulphide*: Manganese sulphide (MnS) belongs to VII–VI compound semiconductor materials. During recent years, dilute magnetic semiconducting materials have become a focus of interest as they exhibit an interesting combination of magnetism and semiconductivity (Lokhande *et al* 1998a). MnS is such a material with band gap energy, $Eg = 3{\cdot}1$ eV, having potential use in solar cell applications as a window/buffer material. The cubic a-phase of MnS appears to be stable above room temperature, but when they turned to a-phase of MnS, they can be prepared at low temperature. The g-phase of MnS can be prepared at low temperature, but they turned to a-phase above 200°C. The a-phase is retained at all temperatures (Madelung 1984; Giriat and Furdyana 1988). The deposition of MnS thin films was carried out by Pathan *et al* (1999a,b). Plots of optical absorption against wavelength (inset) and $(ahn)^2$ against $h\nu$ for SILAR deposited MnS thin films are shown in figure 9.

Manganese disulphide (MnS_2) also belongs to VII–VI compound semiconductor materials. MnS_2 has a golden-yellow colour. The optical band gap is around 3·1 eV. The electrical resistivity of the film is of the order of 10^6–10^7 Ωcm with p-type electrical conductivity. Pyrite type phase of MnS_2 (p-MnS_2) has an anti-ferromagnetic ordering of the third kind (AF_3) below 48 K involving a doubling of the chemical cell in the direction where the moments alternate. MnS_2 could be regarded as an essentially ionic compound. p-MnS_2 is rather compressed with a bulk modulus of 76 GPa, and that a pressure effect includes at about 14 GPa a structure transition from the pyrite to marcasite-type phase accompanied by a large volume concentration (15%). The deposition of MnS_2 has been reported (Pathan *et al* 1999a; Kulkarni *et al* 2002).

5.1m *Ferrous sulphide*: Ferrous sulphide belongs to VIII–VI compound semiconductor materials. The optical band gap of FeS_2 is 3 eV. Due to their high absorption coefficient, (10^5 cm^{-1}) and semiconducting nature, FeS_2 is a promising candidate for ultra thin solar cells, as very little material is needed and the contact materials do not have quality optoelectronic materials. FeS_2 thin films have been deposited by Salunkhe *et al* (1999).

5.1n *Cobalt sulphide*: Cobalt sulphide belongs to VIII–VI compound semiconductor materials. Films are of black colour. Cobalt sulphide (CoS) is a semiconductor with band gap energy equal to 0·9 eV, however, Co_3S_4 has optical band gap of about 0·78 eV. Electrical resistivity of CoS is of the order 10^4–10^6 Ωcm. Cobalt sulphide has potential applications in solar selective coatings, IR detectors and as a storage electrode in photoelectrochemical storage device (Basu and Pramanik 1986). CoS films are deposited by Sartale and Lokhande (2000c).

5.1o *Nickel sulphide*: Nickel sulphide belongs to VIII–VI compound semiconductor materials. It has hexagonal crystal structure. The films are black in colour. The optical band gap is 0·35–0·8 eV. Electrical resistivity is of the order of 10–10^4 Ωcm. Nickel sulphide films have a number of applications in various devices such as solar selective coatings, solar cells, photoconductors, sensors, IR detectors, as an electrode in photoelectrochemical storage device etc (Pramanik and Biswas 1986). The thin films of NiS were deposited by Sartale and Lokhande (2001b).

5.1p *Lanthanum sulphide*: Lanthanum sulphide belongs to III–VI compound semiconductor materials. This system is more complicated in the sense that four well known phases, $La_{1·94}S$, LaS_2, La_2S_3 and La_5S_7, are known to exist by creating lanthanum vacancy. The cubic to tetragonal distortion of the unit cell found in crystal and close to stoichiometric La_3S_4 was of Jahn–Teller band type. The films are yellow in colour. The optical band gap is ~ 2·5 eV. Electrical resistivity is found to be of the order of 10^4–10^5 Ωcm with *p*-type electrical conductivity. La_3S_4 was a strong coupling superconductor with a BCS coherence length, 132 Å. Superconducting (Berkley *et al* 1988), *g*-La_2S_3 films were used in infrared transmitting material for window applications (Kunta *et al* 1993). Thin films and rare earth chalcogenide were used in rare earth alloy preparation, superconducting, magnetic cooling, magnetic thin films, photovoltaic devices, thermoelectric devices, for infrared transmitting window materials etc. The films are deposited by Kulkarni *et al* (2003). Plot of optical absorption against wavelength (inset) and $(ahn)^2$ against *hn* for SILAR deposited lanthanum sulphide thin films is shown in figure 9. Figure 10 shows the plot of log *r* against (1000/*T*) for SILAR deposited lanthanum sulphide thin films.

5.2 *Metal selenide thin films*

5.2a *Copper selenide*: Copper selenide belongs to I–VI compound semiconductor materials. Copper selenide usually exists as copper (I) selenide (Cu_2Se or $Cu_{2-x}Se$) or copper (II) selenide (CuSe or Cu_3Se_2). Cu_3Se_2 is often reported as an impurity phase along CuSe. Copper (I) selenide exists in the cubic, tetragonal, orthorhombic or monoclinic

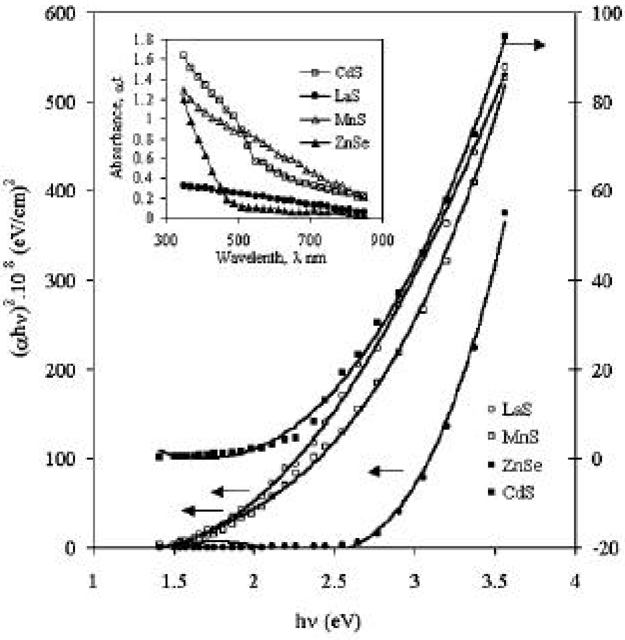

Figure 9. Typical plots of optical absorption against wavelength (inset) and $(ahn)^2$ against *hn* for SILAR deposited CdS, LaS, MnS and ZnSe thin films.

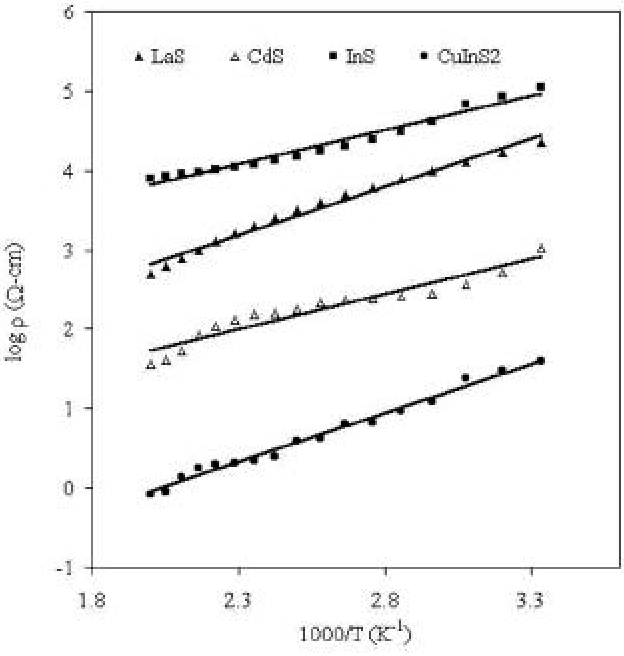

Figure 10. Typical plot of log *r* against (1000/*T*) for LaS, CdS, InS and $CuInS_2$ thin films.

forms. The interest for copper selenide semiconducting thin film is motivated by its application in solar cell technology (Loferski 1956; Okimura *et al* 1980; Chen *et al* 1985). The complexity of composition of copper selenide has always lead to the search for more chemically stable forms with better electronic properties. This material usually exists as a copper (I) selenide (Cu_2Se or $Cu_{2-x}Se$) (Shafizade *et al* 1976; Toneje and Toneje 1981; Padam 1987; Kashida and Akai 1988; Haram *et al* 1992; Levy-Clement *et al* 1997) or copper (II) selenide (CuSe or Cu_3Se_2) (Shafizade *et al* 1978; Mondal and Pramanik 1983, 1984; Estrada *et al* 1994). Copper selenide finds applications as solar cell material and super-ionic conductor (Okimura *et al* 1980; Chen *et al* 1985; Korzhuev 1998). Copper (I) selenide exists in cubic, tetragonal or orthorhombic or monoclinic forms. Orthorhombic copper (I) selenide can be converted to its cubic phase by heating the material or by electrochemical polarization. This phase transition is also possible at room temperature, by controlling the selenium concentration (Haram and Santhanam 1994). The monoclinic/orthorhombic form of b-$Cu_{2-x}Se$ (Eg = 1·4 eV) might be used as a p-type window material for solar cells and the cubic form (a-$Cu_{2-x}Se$) is a high temperature phase (Bickulova *et al* 1995). $Cu_{2-x}Se$ is a semiconductor having cubic $Fm3M$ structure with lattice constant, a = 5·76 Å and is used as a window material in $Cu_{2-x}Se$/Si solar cells. Deposition of Cu_2Se has been reported by Pathan *et al* (2003a). Typical scanning electron micrograph of copper selenide is shown in figure 6(f).

5.2b *Silver selenide*: Silver selenide belongs to I–VI compound semiconductor materials. The films are blackish in colour. The optical band is ~ 1·2 eV. Silver selenide is a well-known super-ionic conductor. It has been used as thermochromic material for non-linear optical devices, photo-chargeable secondary batteries and multipurpose ion-selective electrodes. The deposition of Ag_2Se was carried out by Pathan and Lokhande (2001b).

5.2c *Zinc selenide*: Zinc selenide belongs to II–VI compound semiconductor materials. It has cubic and/or hexagonal crystal structure. The films are yellow-orange in colour. The optical band is 2·6–3·1 eV. The electrical resistivity is of the order of 10^4–10^{12} Ωcm. The film shows n-type electrical conductivity. ZnSe has several advantages: the band gap of ZnSe (2·67 eV) is wider than that of the CdS (2·42 eV) and allows transition of higher energy photons compared to CdS. In addition, ZnSe has a better lattice match with $Cu(InGe)Se_2$ thin film absorber in band gap range 1·3–1·5 eV. ZnSe is semiconducting that has large potential applications in thin films like photoluminescence and electroluminescent devices and as an n-type window layer for thin film heterojunction solar cells. ZnSe is an attracting material as based solar cells, as it is Cd free (Lokhande *et al* 1998b). It is also used in IR optics, scintillater and substrate modulators. The deposition of ZnSe was carried out by Sankapal *et al* (1999b). Plots of optical absorption against wavelength (inset) and $(ahn)^2$ against hn for SILAR deposited ZnSe thin film are shown in figure 9.

5.2d *Cadmium selenide (CdSe)*: CdSe is a II–VI semiconductor compound. It has wurtzite (hexagonal) and/or cubic crystal structure. The density of CdSe is 5·674 g/cm^3. The optical band gap is 1·7 eV. The electrical resistivity is of the order of 10^4 Ωcm. The film shows n-type electrical conductivity. Cadmium selenide has shown great promise as a photo-conductor and solar energy material. These films have applications in manufacture of electronic devices: thin film transistors and g-ray detectors. It is also used in IR optics, polarizers, substrates, detectors and sources for vacuum deposition. The deposition of cadmium selenide thin film using SILAR method was carried out by Sankapal *et al* (1999c).

5.2e *Indium selenide*: Indium selenide belongs to III–VI compound semiconductor materials. In_2Se_3 is a complex hexagonal layered semiconductor with a direct band gap of 1·42 eV and an indirect band gap of 1·29 eV. The electrical resistivity is of the order of 10^7 Ωcm with n-type electrical conductivity. In_2Se_3 have been grown recently and characterized for making positive electrodes in new micro-devices like capacitors or micro-batteries with solid electrolytes exhibiting fast ionic conductivity (Kleitz *et al* 1983). It is of interest because of its polymorphism and related metal ion defect structure. In_2Se_3 exhibits atleast three different crystalline modifications denoted as a, b and g transition, temperature of 200 and 650°C, respectively for $a \to b$ and $b \to g$ transition (Ballkanski *et al* 1983). The films were deposited by Pathan and Lokhande (2003b).

5.2f *Antimony selenide*: Antimony selenide belongs to V–VI compound semiconductor materials. Antimony trisulphide is layer-structured semiconductor with orthorhombic crystal structure. Sb_2Se_3 thin films have attracted wide attention, due to their good photovoltaic properties and high thermoelectric power (TEP), which allow possible applications for optical and thermoelectric cooling devices. The specific resistance of amorphous Sb_2Se_3 is of the order of 10^7 Ωcm with an optical band gap of 1·88 eV. The crystal structure of Sb_2Se_3 is orthorhombic. Antimony trisulphide semiconductor thin films were used to improve efficiency and stability in PEC solar cell configuration. The deposition of antimony selenide was carried out by Sankapal *et al* (2000d). X-ray diffraction pattern of Sb_2Se_3 films deposited onto amorphous glass is shown in figure 5b (ii). It was observed that films onto amorphous glass substrate are nanocrystalline consisting of fine grains. 2D and 3D AFMs of Sb_2Se_3 film are shown in figure 7(e). The films appear to be made up of fine particles or nanoparticles.

5.2g *Bismuth selenide*: Bismuth triselenide is a member of V–VI compound semiconductors. It has hexagonal crystal structure. The optical band gap is around 0·35 eV. Electrical resistivity is of the order of 10^5 Ωcm. It continues to draw considerable interest because of its applications in various fields. In recent years considerable attention has been focused on glasses of Bi and Se because of their use in optical and photosensitive devices. Over last two decades, many experimental data have been gathered on electrical, optical and thermoelectrical properties of bismuth material, owing to its applications such as presence of temperature control of laser diode etc (Watanbe *et al* 1983; Mandal and Savadogo 1991; Yesgude *et al* 1995). The deposition was carried out by Sankapal *et al* (2000e). X-ray diffraction pattern of Bi_2Se_3 films deposited onto amorphous glass is shown in figure 5b (i). It was observed that films deposited onto amorphous glass substrate are nanocrystalline consisting of fine grains. Figure 7 shows the 2D and 3D AFMs of Bi_2Se_3 film. The film appears to be made up of fine particles or nanoparticles.

5.2h *Lanthanum selenide*: Lanthanum selenide belongs to III–VI compound semiconductor materials. The optical band gap of lanthanum selenide is ~ 2·45 eV. Electrical resistivity is of the order of 10^4 Ωcm with *p*-type electrical conductivity. Lanthanum selenide shows remarkably sharp possible peak at 2·1° at 2·77 eV and a broader and smaller structure at 3·01 eV. Since the discovery of high temperature superconductors, great efforts have been made to deposit high quality lanthanum selenide in thin film form. The films are of great interest for application in magnetic, optical, nuclear, semiconductor, photoelectrochemical cells, cold cathode emitter devices, infrared materials, window device formation, electrical switching etc. The films were deposited by Pathan *et al* (2002a).

5.3 *Metal telluride thin films*

5.3a *Copper telluride*: Copper telluride belongs to I–VI compound semiconductor materials. Copper telluride [Cu_xTe] has different crystal structures depending upon the value of x as an orthorhombic, cubic and tetragonal crystal structure. Generally the films are blue–purple–red in colour. Copper telluride forms different phases viz. CuTe, $Cu_{2-x}Te$, $Cu_{1·8}Te$, Cu_2Te etc. Cu_xTe thin films have been found to possess near ideal solar control characteristics. The Cu_xTe thin films may be used in photo-detectors and in photovoltaic applications. Pathan *et al* (2003b) have investigated the deposition of Cu_2Te using SILAR method.

5.3b *Cadmium telluride*: Cadmium telluride belongs to II–VI compound semiconductor materials. It has cubic zincblende crystal structure. Cadmium telluride receives much attention as absorber material for efficient low cost solar cells. Their advantages include high absorption coefficient, direct band gap with nearly optimum value of the photovoltaics and good match of the electron affinity efficiency as high as 16% have been reported and the maximum theoretical efficiency was estimated to be 29%. Also the growth of high quality CdTe is important because of its potential applications in solar energy, X-ray detection, *g*-ray detection, IR optics, substrates, detectors and crystal pieces for vacuum deposition etc. The deposition of cadmium telluride thin films was carried out by Lokhande and Pathan (2001b).

5.3c *Indium telluride*: Indium telluride is a member of III–VI group semiconducting materials. It (In_2Te_3) has face centred cubic or hexagonal crystal structure, whereas InTe has tetragonal or cubic crystal structure. The films are blue-grey in colour. The electrical resistivity is around 10^5 Ωcm with *n*-type electrical conductivity. In_2Te_3 may be used as a buffer layer in $Cu(In,Ga)Se_2$ based solar cells and making positive electrodes in new micro-devices like capacitors or micro-batteries. The deposition of indium telluride thin films was carried out by Pathan and Lokhande (2003b). Scanning electron micrograph of indium telluride is shown in figure 6. The films look smooth and homogeneous without visible pores.

5.3d *Lanthanum telluride*: Lanthanum telluride belongs to III–VI compound semiconductor materials. It has cubic crystal structure. The optical band gap is ~ 2·4 eV. Electrical resistivity is of the order of 10^4–10^5 Ωcm with *p*-type electrical conductivity. Single crystal of $LaTe_2$ showing a black metallic luster was obtained which measured up to several mm in length and width. The existence of solid-solubility indicates that an ion-covalent bonding mechanism rather than a purely metallic bond exists in this compound. The deposition of lanthanum telluride thin films was carried out by Pathan *et al* (2002a).

5.4 *Metal oxide thin films*

5.4a *Copper oxide*: Copper oxide belongs to I–VI compound semiconductor material. Cu_2O is *p*-type which has a direct optical band gap of 2 eV. Cuprous oxide, red copper oxide (Cu_2O), a non-toxic material, is potentially attractive as an active solar cell material, selective absorber layer and used in oxygen or humidity sensors (Olsen *et al* 1983; Rai 1988; Ristov *et al* 1988). Many workers have carried out the deposition of copper oxide (Ristov *et al* 1985; Tolstoi and Molotilkina 1994; Nair *et al* 1999) using SILAR method.

5.4b *Zinc oxide*: Zinc oxide belongs to II–VI compound semiconductor materials. It has wurtzite crystal structure. The optical band gap is ~ 3·3 eV. It has high optical transmittance (> 80%) in the visible range of radiation. It is thermally as well as chemically stable over

Table 1. Deposition conditions and properties of metal chalcogenide thin films deposited by SILAR method.

Sr. no.	Precursors		Temp (°C)	Subs	Ad	Ri	Re	Cy	Th. (μm)	Remarks	Ref.
	Cationic	Anionic									
5.1 Metal sulphide thin films											
5.1a Copper sulphide											
i	0·1 M $CuSO_4 + NH_3$ (pH ~ 10)	0·1 M $H_2N{\cdot}CS{\cdot}NH_2$ (pH ~ 6)	27	Glass, Si (111)	20	30	20	25	0·4	The formed compound was a mixture of Cu_xS with $1{\cdot}83 \le x \le 1{\cdot}96$ and Cu_2S phases with hexagonal crystal structure. The optical band-gap was found to be 2·36 eV. The electrical resistivity was of the order of 10^{-2} Ω-cm with *p*-type electrical conductivity. The growth rate was found to be 16 nm/cycle.	Sartale and Lokhande (2000a)
ii	6·25–50 mM $Cu(CH_3COO)_2$ (pH ~ 5·3–5·7)	3–25 mM Na_2S (pH ~ 11)	27	Glass, ITO, CdS	5 to 20	75 to 125	5 to 20	–	–	The depositions were carried out in N_2 atmosphere. The films were polycrystalline and hexagonal CuS. Stoichiometry of all the Cu_xS films was Cu_xS ($x = 1$). The Cu_xS spectrum showed low transmission above 800 nm and peak transmission close to 600 nm. The surface of Cu_xS was rough compared with CdS films.	Lindroos *et al* (2000)
iii	0·12 M $CuSO_4$ + TEA +HH (pH ~ 5)	0·05 M Na_2S (pH ~ 12)	27	Glass	30	50	30	60	0·44	The formed compound was single phase of Cu_2S with hexagonal crystal structure. The films were found to exhibit maximum transmittance ~ 53·4% for $\lambda = 630$ nm. The absorption of film was 10^4 cm^{-1}. The band gap was 2·33 eV with *p*-type electrical conductivity. The films were found to be nanocrystalline. The growth rate of the film was estimated to be 7 nm/cycle.	Pathan *et al* (2001a)
5.1b Silver sulphide											
	0·05 M $AgNO_3$ + EDTA (pH ~ 8)	0·4 M $H_2N{\cdot}CS{\cdot}NH_2$ (pH ~ 6)	27	Glass, Si (111)	12	10	12	15	0·22	The crystallinity was improved significantly with Si (111) substrate. Annealing of films in air resulted in increase in intensities of existing planes. SEM showed that etched films were homogeneous and uniform. The optical band-gap and electrical resistivity were found to be 1·1 eV and 10^4 Ω-cm, respectively. Photoelectrochemical study showed that the films were photoactive and of *n*-type electrical conductivity. The growth rate of the film was 14 nm/cycle.	Sankapal *et al* (2002a), Pathan *et al* (2001a)
5.1c Zinc sulphide											
i	5 mM–5 M $ZnSO_4$, $ZnCl_2$ (pH ~ 3·7)	5 mM Na_2S (pH ~ 12)	–	ITO, Mo	–	–	–	–	–	Electro-kinetic potential measurement as a function of concentration and pH of reaction solution was discussed. Thickness of the films was estimated *in situ* from the interference colours of the films. Refractive index was found to be $n = 2{\cdot}2$ for 623 nm film. The structure of the film on ITO coated glass and on Mo was polycrystalline cubic having a poor (111) preferred orientation. Films were non-porous and with small grains (45 to 65 nm).	Nicolau and Minnard (1988)
ii	0·1 M $ZnCl_2$ + 0·3 M TEA or EN (pH ~ 7·7–8·1) and 0·1 M $ZnCl_2$ + 0·2 M TEA (pH ~ 4·5)	Na_2S (pH ~ 12)	27	Glass, ITO	20	100–200	20	–	–	Influence of the complexing agents on the morphology and structural properties of deposited film was discussed. The growth was found to be different, for different substrates. The growth rate varied between 0·13 and 0·27 nm/cycle. Annealing slightly improved the quality of ZnS films. The high refractive indices (1·95–2·23) and packing densities were found (72–90%) in films grown on ITO with TEA complexed. The Zn : S ratio in the film was 0·8–0·89. The films were polycrystalline and presumably cubic.	Lindroos *et al* (1998)
iii	0·1–0·2 M $ZnCl_2$ (pH ~ 5·0–5·3)	0·05–0·1 M Na_2S (pH ~ 12)	27	Polyester	20	120	20	–	–	The films on polyester substrates prepared with $SnCl_2$ solution were amorphous up to ~ 250 nm thickness and above that thickness of the film was found to be polycrystalline. The optical band gap was found to be 3·44 eV.	Lindroos *et al* (1997)

Sr. no.	Precursors		Temp (°C)	Subs	Ad	Ri	Re	Cy	Th. (μm)	Remarks	Ref.
	Cationic	Anionic									
										The transmittance was more than 60% above 400 nm. The growth rate was 0·16 nm/cycle for 0·1 M $ZnCl_2$ and 0·1 M Na_2S and 0·22 nm/cycle when concentration was doubled. EDAX showed Zn : S ratio (wt%) varied from 1·05–1·23. Film consisted of 7–16% oxygen. The growth of ZnS on polyester was found to be higher than films deposited on glass, GaAs and ITO substrate using SILAR method.	
iv	0·1 M $ZnSO_4$ + NH_3 (pH ~ 10)	0·1 M Na_2S (pH ~ 12)	27	Glass, quartz	10	15	10	90	0·25	The growth rate was found to be 20 nm/cycle. The film consisted of Zn, O, S i.e. $Zn_x(O,S)_y$. The band gap of the film was found to be 3·30 eV which lies between the band gap of ZnS and ZnO. The electrical resistivity was of the order of 10^6 Ω-cm.	Lokhande *et al* (2002)
v	0·1 M $ZnCl_2$ 0·01 M $MnCl_2$	50 mM Na_2S	27	Glass, ITO, Al_2O_3, quartz, CaF_2	20	20	20	165	0·25	The ZnS films were polycrystalline with cubic structure. The as deposited ZnS : Mn films were uniform but slightly less smooth compared with undoped ZnS films. The Mn level in ZnS film was 0·3 to 0·8 wt% using MnS/ZnS cycle 1 : 100 was achieved. The growth rate was 0·09 nm/cycle. Refractive indices varied from 2·04–2·22 and 2·13–2·32 on glass and ITO substrates, respectively. ZnS : Mn films contained ~ 20 at % oxygen and 3–15 at % hydrogen, but due to annealing their contents were significantly reduced.	Lindroos *et al* (1995)
5.1d	Cadmium sulphide										
i	5 mM $CdSO_4$ (pH ~ 8)	5 mM Na_2S (pH ~ 11·6)	27	Glass, FTO, Si, Mo, Ti, Ge, GaAs, InP, $LiNbO_3$, CaF_2	40	100	40	–	–	Water flow rate was 30 l/h and N_2 flow rate was 50 l/h. Epitaxial films have been grown on InP, Ge, and GaAs. Polycrystalline hexagonal CdS films of optical quality have been obtained on $LiNbO_3$, FTO-glass, Mo, Ta and Ti. CdS films of poor quality, inhomogeneous and irreproducible have been obtained on Si and CaF_2.	Nicolau (1985)
ii	5 mM $CdSO_4$, $CdCl_2$	5–2·8 mM Na_2S		ITO, Mo, InP	–	–	–	–	–	Electro-kinetic measurement as a function of concentration and pH of reactant solution was discussed. CdS films grown on (111) InP shows differently oriented grains. Films were of hexagonal type. The structure of CdS film deposited on ITO coated glass and Mo was polycrystalline with strong (001) preferred orientations of stratified grains. The films have larger grain size from 30–60 nm. The N_2 flow inside bell jar was kept at 10 l/min.	Nicolau and Minnard (1988)
iii	0·125 M $CH_3(COOH)_2$ Cd (pH ~ 5) 1 M $CH_3(COOH)_2$ Cd (non-aqueous)	0·05 M Na_2S (pH ~ 12) 1 M $H_2N{\cdot}CS{\cdot}NH_2$ (non-aqueous)	30	Glass	20	20	20	160	0·28	The films were deposited from aqueous and non-aqueous media. Films were amorphous with hexagonal crystal structure. SEM shows that the films were dense, smooth and homogenous without visible porous. Small nanoparticles with diameters 7–8 nm and 6–7 nm were clearly recognized for films from aqueous and non-aqueous medium, respectively. RBS spectra concluded that the films were in well stoichiometric for both the samples along with presence of oxygen.	Lokhande *et al* (2001)
iv	0·025 M $CH_3(COOH)_2$ Cd (pH ~ 5)	0·1 M Na_2S (pH ~ 9)	80	Glass	15	10	15	20	28	As deposited films were amorphous with hexagonal structure. Annealing in nitrogen atmosphere improved the crystallinity of film. The films were homogenous and covered the substrate well. The slight decrease in optical	Sankapal *et al* (2000e)

Sr. no.	Precursors		Temp (°C)	Subs	Ad	Ri	Re	Cy	Th. (μm)	Remarks	Ref.
	Cationic	Anionic									
										band gap (2·24–2·17 eV) and electrical resistivity (0·419 × 10^5 – 0·125 × 10^5 Ω-cm) were found for annealed films at 673 K.	
v	0·2 M $CdCl_2$ (pH ~ 5)	0·1 M Na_2S (pH ~ 12)	27	ITO, GaAs	40	100–150	40	–	–	The deposition was carried out in N_2 atmosphere. The nominal growth rates were 0·13 and 0·078 nm/cycle for the films deposited on ITO and GaAs (100) substrates, respectively. The films on both the substrates were found to be polycrystalline and strongly textured. The surface looked smooth and uniform. The average stoichiometry of CdS on ITO was Cd 49 and S 51 at %.	Valkonen *et al* (1997a,b)
vi	5 mM $CH_3(COOH)_2$ Cd (pH ~ 4·5) and 10 mM $CH_3(COOH)_2$ Mn (pH ~ 5)	5 mM Na_2S (pH ~ 12)	27	Glass, FTO	20	20	20	165	0·25	After Mn doping, crystallinity of CdS was increased. Observed "*d*" values were slightly different than standard "*d*" values of CdS. Optical band gap was 2·26 eV for CdS and 2·7 eV for Mn doped CdS.	Kulkarni *et al* (2002)
5.1e	Indium sulphide										
i	0·04 M $InCl_3$ (pH ~ 4)	0·1 M Na_2S (pH ~ 8)	27	Glass	20	–	15	50	0·3	The films were nanocrystalline with cubic structure. The optical band gap was 2·3 eV. The electrical resistivity was of the order of 10^5 Ω-cm with *n*-type electrical conductivity.	Pathan *et al* (2001b)
ii	0·08 M $In_2(SO_4)_3$ (pH ~ 5)	0·1 M Na_2S (pH ~ 12)	27	Glass	30	50	30	60	0·37	The films were nanocrystalline with mixed phases of InS, In_2S_3 and In_6S_7. The film has direct optical band gap of 2·7 eV with *n*-type electrical conductivity. The film exhibits high optical absorbance (10^4 cm^{-1}).	Pathan *et al* (2001b) Lokhande and Pathan (2001a)
5.1f	Tin sulphide										
	0·2 M $SnCl_2$ (pH ~ 2)	0·1 M Na_2S (pH ~ 9)	27	Glass, Si (111)	20	10	20	125	1·0	SnS_2 films on glass were amorphous or consist of fine grains, while those on Si (111) were strongly textured with hexagonal crystal structure. The optical band gap energy was found to be 2·6 eV. The electrical resistivity was of the order of 10^3 Ω-cm. The film showed *n*-type electrical conductivity.	Sankapal *et al* (2000c)
5.1g	Lead sulphide										
	0·1 M $CH_3(COO)_2$ Pb + TEA (pH ~ 7·8))	0·1 M CH_3CSNH_2 (pH ~ 4·8)	27	Glass	20	80	40	800	0·004	The films were polycrystalline and highly (100) oriented. The films looked (thickness, – 30 nm) continuous but grainy, clearly consist of separate particles. LFM have been used to distinguish local surface properties also. LFM and FM have been used to obtain information about surface coverage.	Kanniainen *et al* (2000) Resch *et al* (1997)
5.1h	Arsenic sulphide										
i	0·1 M As_2O_3 + EDTA (pH ~ 1)	0·1 M $Na_2S_2O_3$	80	Glass, Si (111)	15	10	15	50	0·3	The films were yellowish in colour and well adherent to the substrates. The films deposited on glass substrates were amorphous whereas those on Si (111) wafer substrate were polycrystalline with monoclinic structure. The bandgap and electric resistivity were found to be 2·38 eV and 10^5 Ω-cm, respectively.	Sartale and Lokhande (2000b)
5.1i	Antimony sulphide										
i	0·2 M Sb_2O_3 + TA (pH ~ 6)	0·3 M $Na_2S_2O_3$	50 (± 1)	Glass	20	10	20	14	0·78	The films were amorphous or consist of fine grain with an orthorhombic crystal structure. The optical band gap was 1·8 eV. The electrical resistivity was of the order of 10^7 Ω-cm.	Sankapal *et al* (1999a)

Sr. no.	Precursors		Temp (°C)	Subs	Ad	Ri	Re	Cy	Th. (μm)	Remarks	Ref.
	Cationic	Anionic									
5.1j	Bismuth sulphide										
	0·003 M $Bi(NO_3)_3$ + TEA (pH ~ 9)	0·1 M CH_3CSNH_2 (pH ~ 11)	27	Glass	20	40	20	20	0·14	As deposited films were amorphous. After annealing films turned from amorphous to polycrystalline, the optical band gap and electrical resistivity for as deposited film were found to be 1·78 eV and 10^4 Ω-cm, respectively. Film showed *n*-type electrical conductivity.	Ahire *et al* (2001a,b)
5.1k	Molybdenum disulphide										
	0·001 M $(NH_4)_6$ Mo_7O_{24} + HCl (pH ~ 3)	0·2 M Na_2S (pH ~ 13·5)	27	Glass, FTO, Si(111)	25	30	25	100	0·2	The formed material was MoS_2 with hexagonal crystal structure. The films formed on glass were nanocrystalline whereas films onto FTO and Si (111) were microcrystalline. The optical bandgap was found to be 1·74 eV. The electrical resistivity was of the order of 104 Ω-cm with *p*-type electrical conductivity.	Sartale and Lokhande (2001a)
5.1l	Manganese sulphide										
i	0·3 M $CH_3(COO)_2Mn$ (pH ~ 8)	0·1 M Na_2S (pH ~ 12)	27	Glass	20	40	20	60	0·33	The films were of MnS_2 with cubic crystal structure. The optical band gap was found to be 3·1 eV. The electrical resistivity was of the order of 10^6 Ω-cm with *p*-type electrical conductivity. No significant change was observed after annealing the films in air for 30 min.	Pathan *et al* (1999a)
ii	0·1 M $MnSO_4$ (pH ~ 6)	0·1 M Na_2S (pH ~ 12)	27	Glass	20	40	20	55	0·36	The films were of MnS_2 with cubic crystal structure. The optical band gap was found to be 2·9 eV. The electrical resistivity was of the order of 10^5 Ω-cm with *p*-type electrical conductivity. The film showed significant increase in crystallinity after annealing the films at 300°C for 30 min.	Pathan *et al* (1999b)
iii	0·01 M $CH_3(COO)_2Mn$ (pH ~ 5)	0·005 M Na_2S (pH ~ 12)	27	Glass, Mo, FTO	20	20	20	150	–	The films were MnS. The optical band gap was 2·9 eV and electrical resistivity was of the order of 10^5–10^6 Ω.cm with *p*-type electrical conductivity.	Kulkarni *et al* (2002)
5.1 m	Ferrous sulphide										
	0·4 M Ferric citrate + TEA + HH (pH ~ 10·5)	0·1 M Na_2S (pH ~ 8·5)	27	Glass	10	30	10	60		The films were found to be amorphous. Films were annealed up to 673 K for 30 min, however no significant change was observed. The band gap was found to be 1·1 eV with electrical resistivity of the order of 10^3 Ω-cm.	Salunkhe *et al* (1999)
5.1n	Cobalt sulphide										
	0·02 M $CoSO_4$ + NH_3 (pH ~ 8)	0·05 M Na_2S (pH ~ 12)	27	Glass, Si (111)	50	75	50	25	–	Thin films deposited onto glass substrates were amorphous whereas those deposited onto Si (111) wafer were polycrystalline. The band gap was found to be of the order of 10^4 Ω-cm with *p*-type electrical conductivity.	Sartale and Lokhande (2000c)
5.1o	Nickel sulphide										
	0·1 M $NiSO_4$ + NH_3 (pH ~ 8)	0·5 M Na_2S (pH ~ 10)	27	Glass, FTO, Si(111)	60	40	60	150	0·1	The formed material was NiS with hexagonal crystal structure. The film was homogeneous, fine and well covered to the substrate with overgrowth of some particles. The optical band gap equal to 0·45 eV was observed. The electrical resistivity was of the order of 10 Ω-cm.	Sartale and Lokhande (2001b)
5.1p	Lanthanum sulphide										
	0·1 M $LaCl_3$ (pH ~ 3)	0·1 M Na_2S (pH ~ 12)	27	Glass	20	70	20	140	0·1	The films were nanocrystalline with La_5S_7 and La_2S_3 phases. The optical band gap was found to be 2·6 eV. Electrical resistivity was of the order of 10^5 Ω-cm with *p*-type electrical conductivity.	Kulkarni *et al* (2003)

Sr. no.	Precursors		Temp (°C)	Subs	Ad	Ri	Re	Cy	Th. (μm)	Remarks	Ref.
	Cationic	Anionic									
5.2 Metal selenide thin films											
5.2a Copper selenide											
	0·12 M $CuSO_4$ + TA (pH ~ 3)	0·05 M Na_2SeSO_3 (pH ~ 12)	27	Glass	30	50	10	65	0·33	The deposited films were nanocrystalline with single phase of Cu_2Se. The films have direct band gap of 2·18 eV. The electrical resistivity was of the order of 10^{-2} Ω-cm with *p*-type electrical resistivity.	Pathan *et al* (2003a)
5.2b Silver selenide											
	0·05 M $AgNO_3$ (pH ~ 4)	0·1 M Na_2SeSO_3 (pH ~ 12)	27	Glass	20	50	20	30	0·25	The films were nanocrystalline. The optical band gap of the film was found to be 1·3 eV.	Pathan *et al* (2001b)
5.2c Zinc selenide											
	0·2 M $CH_3(COO)_2Zn$	0·1 M Na_2SeSO_3	27	Glass, FTO, Si(111), GaP (111)	10	10	10	–	–	Annealing of the film at 200°C showed improvement in crystallinity. The optical band gap was found to be 2·6 eV. The electrical resistivity was of the order of 10^4 Ω-cm.	Sankapal *et al* (1999b)
5.2d Cadmium selenide											
	0·2 M $CdSO_4$ + TA	0·1 M Na_2SeSO_3 (pH ~ 12)	27	Glass, FTO	30	30	30	80	–	Formed films were CdSe with hexagonal crystal structure. The average ratio of at% of Cd : Se was 55 : 45. The optical band gap of film was found to be 1·80 eV. The electrical resistivity was of the order of 10^4 Ωcm. The film showed *n*-type electrical conductivity.	Sankapal *et al* (1999c)
5.2e Indium selenide											
	0·1 M $In_2(SO_4)_3$ (pH ~ 3)	0·05 Na_2SeSO_3 (pH ~ 12)	27	Glass	30	50	10	65	0·41	The films on glass substrates were amorphous or consisting of fine grains with InSe, In_2Se_3 and In_6Se_7 phases. The optical band gap energy was found to be 2·6 eV. The electrical resistivity was of the order of 10^6 Ω-cm. The films show *n*-type electrical conductivity.	Pathan *et al* (2003b)
5.2f Antimony selenide											
	0·2 M Potassium antimony tartrate (pH ~ 5)	0·1 M Na_2SeSO_3 (pH ~ 12)	27	Glass	60	40	60	–	–	The films were nanocrystalline. The optical band gap was 1·7 eV with electrical resistivity of the order of 10^5–10^6 Ω-cm.	Sankapal *et al* (2000d)
5.2g Bismuth selenide											
	0·1 M Bismuth nitrate + TEA (pH ~ 8)	0·1 M Na_2SeSO_3 (pH ~ 10·5)	27	Glass, Si (111)	30	30	30	25	0·18	The film deposited on Si (111) showed improvement in crystallinity compared to the films on the glass substrates. The optical band gap was found to be 0·38 eV. The electrical resistivity was of the order of 10^5 Ωcm. The decrease in electrical resistivity was observed after annealing the films. The average grain size was 5–6 nm. PEC study confirmed *n*-type electrical conductivity of the material.	Sankapal *et al* (2000e)
5.2h Lanthanum selenide											
	0·1 M $LaCl_3$ + TA (pH ~ 3)	0·1 M Na_2SeSO_3 (pH ~ 12)	27	Glass	20	60	20	35	0·25	Films were nanocrystalline with $LaSe_2$, La_2Se_3 and La_3Se_4 phases. The optical band gap was 2·4 eV. The electrical resistivity was of the order of 10^4 Ω-cm with *p*-type electrical conductivity.	Pathan *et al* (2002a)
5.3 Metal telluride thin films											
5.3a Copper telluride											
	0·08 M $CuSO_4$ (pH ~ 5)	0·05 M Na_2TeO_3 (pH ~ 3)	27	Glass	20	50	20	50	0·36	Films consist of $Cu_{2-x}Te$ and Cu_2Te phases. The optical band gap was ~ 2·2 eV. Electrical resistivity was of the order of 10 Ω-cm with *p*-type electrical conductivity.	Pathan *et al* (2003b)

Sr. no.	Precursors		Temp (°C)	Subs	Ad	Ri	Re	Cy	Th. (μm)	Remarks	Ref.
	Cationic	Anionic									
5.3b	Cadmium telluride										
	0·1 M $CdSO_4$	0·1 M Na_2TeO_3	27	Glass	15	30	15	30	0·26	The films were light grey in colour. Films were hexagonal and cubic structure. The electrical resistivity was of the order of 10^6 Ω-cm.	Lokhande and Pathan (2001b)
5.3c	Indium telluride										
	0·08 M $In_2(SO_4)_3$ (pH ~ 5)	0·05 M Na_2TeO_3 (pH ~ 3)	27	Glass	20	50	20	50	–	The films consist of single phase of In_2Te_3.. The optical band gap of the material was found to be 1·66 eV. The electrical resistivity was of the order of 10^{-1} Ω-cm.	Pathan and Lokhande (2003b)
5.3d	Lanthanum telluride										
	0·08 M, $LaCl_3$ (pH ~ 3)	0·05 M Na_2TeO_3 (pH ~ 3)	27	Glass	30	50	30	45	–	A single phase of La_2Te_3 was observed. Optical band gap was ~ 2·1 eV. Electrical resistivity was of the order of 10^5 Ω-cm with *p*-type electrical conductivity.	Pathan *et al* (2002a)
5.4	Metal oxide thin films										
5.4a	Copper oxide										
i	$CuSO_4$ and $Na_2S_2O_3$	NaOH	Temp. cationic = R.T. Temp. anionic ~ 60–80	Glass	1–2	–	1–2	–	0·2	The as-deposited films are polycrystalline and chemically pure Cu_2O. The absorption spectrum shows a fundamental absorption edge at 2·0 eV. Cu_2O films show photoconductivity.	Ristov *et al* (1985)
ii	$CuSO_4$ and $Na_2S_2O_3$	NaOH	Temp. cationic = R.T. Temp. anionic ~ 50–90	Glass	20	20	20	–	0·45	The as-deposited films are of cupric structure with Cu_2O composition. Annealing the films in air at 300°C converts these films to CuO. This conversion is accompanied by a shift of the optical band gap from 2·1 eV (direct) to 1·75 eV (indirect). The films show *p*-type conductivity, 5×10^4 Ω.cm for a film of thickness 0·15 μm.	Nair *et al* (1999)
iii	Cu salt	H_2O_2/NH_3	20	Si	–	–	–	–	0·22	As-deposited films are of $CuO_2 \cdot nH_2O$.	Tolstoy and Molotilkina (1994)
5.4b	Zinc oxide										
i	Zn salt	H_2O	Temp. cationic = R.T. Temp. anionic ~ 95–100	Glass, quartz, mica	–	–	–	–	0·8	As-deposited films are polycrystalline.	Ristov *et al* (1987)

Sr. no.	Precursors		Temp (°C)	Subs	Ad	Ri	Re	Cy	Th. (μm)	Remarks	Ref.
	Cationic	Anionic									
ii	1 M $ZnSO_4$ + 15 M $NH_4(OH)$	Water	–	Glass	–	–	–	35	0·11	The as deposited film showed hexagonal (*Zincite*) structure with preferred orientations along *c*-axis perpendicular to the glass substrate. The film showed optical band gap, $Eg = 3{\cdot}42$ eV. Computerized electroneumatic deposition system was utilized.	Jim´enez-Gonz´alez and Nair (1995), Jim´enez-Gonz´alez and Su´arez-Parra (1996), Jim´enez-Gonz´alez (1997)
iii	Zn salt	H_2O	Temp. cationic = R.T. Temp. anionic ~ 95–100	Glass	–	–	–	–	> 7	As-deposited films are of ZnO and $Zn(OH)_2$ for films with > 1 μm	Mitra *et al* (1998a,b), Chatterjee *et al* (1999)
iv	Zn salt	H_2O_2/NH_3	20	Si	–	–	–	–	0·014	As-deposited films are of $ZnO_{2-x}{\cdot}nH_2O$.	Tolstoy and Molotilkina (1994)
v	Zn salt	H_2O_2/KOH	20	SiO_2, Ni, PVC, polycarbonate	–	–	–	–	0·06	As-deposited films are of $ZnO_{2-x}{\cdot}nH_2O/Zn(OH)_2$	Lindroos and Leskela (2000)
5.4c	Manganese oxide										
i	Mn $(CHCOOH)_2$, $MnCl_2$ and $Mn(NO_3)_3$	$KMNO_4$	20	Si (111)	–	–	30	–	0·015	As-deposited films are amorphous. The multistage mechanism of layer formation is proposed.	Tolstoy *et al* (1997)
5.4d	Cerium oxide										
i	$Ce(NO_3)_3$ $Ce(CH_3COOH)_2$	H_2O_2/NH_3	20	Si (111), fused quartz	10 min	30	0·25 to 2 min	60	0·3	As-deposited films are amorphous. IBM-compatible computer system was utilized for deposition. The sample do lose water when heated in air at 200°C.	Tolstoy and Ehrlich (1997), Tolstobrov *et al* (2000)
5.5	Ternary sulfide thin films										
5.5a	Copper indium sulphide										
i	0·12 M $CuSO_4$ + TEA + HH (pH ~ 5) and 0·08 M $In_2(SO_4)_3$ + TEA + HH (pH ~ 5)	0·05 M Na_2S (pH ~ 12)	27	Glass	30	50	30	60	0·45	The multilayer CuS–InS films were deposited to form $CuInS_2$. The films were nanocrystalline. The optical band gap was found to be 1·65 eV. The electrical resistivity was found to be of the order of 10^3 Ω-cm.	Pathan *et al* (2001a) Pathan (2002)
ii	0·1 M $CuSO_4$ + 0·08 M $In_2(SO_4)_3$ + TEA + HH (pH ~ 5)	0·1 M Na_2S (pH ~ 12)	27	Glass, FTO	30	50	30	110	0·48	The films consist of $CuInS_2$ and $CuIn_5S_8$ phases. The films were nanocrystalline. The optical band gap was found to be 1·55 eV. The electrical resistivity was found to be of the order of 10 Ω-cm.	Pathan (2002), Pathan and Lokhande (2003a)

Sr. no.	Precursors		Temp (°C)	Subs	Ad	Ri	Re	Cy	Th. (μm)	Remarks	Ref.
	Cationic	Anionic									
5.5b	Cadmium zinc sulphide										
i	0·3 M CdCl$_2$ (pH ~ 5·1) 0·4 M ZnCl$_2$ (pH ~ 5·3)	0·1 M Na$_2$S (pH ~ 12·5)	27	Glass, ITO	20 40	100 150	20 40	–	–	In multilayer CdS/ZnS thin films, both constituents had cubic structure and (111) was the most intensive reflection. Also, (220) reflection of ZnS and (222) of CdS were observed. The sample contained Cd 11%, zinc 39% and sulphur 50 at %. In the CdS/ZnS structure the cations do not diffuse from layer to layer but separate films were detected.	Nicolau *et al* (1990)
5.5c	Cadmium indium sulphide										
	0·1 M CdSO$_4$ (pH ~ 8) and 0·04 M InCl$_3$	0·05 M Na$_2$S (pH ~ 12)	80	Glass, FTO	15	10	15	–	0·44	The films were nanocrystalline with cubic structure. The film annealed at 573 K for 15 min showed improved crystallinity. The optical band gap was found to be 2·12 eV. The electrical resistivity was of the order of 10^4 Ω-cm with *n*-type electrical conductivity.	Pathan *et al* (2001c)
Ternary selenide thin films											
5.5d	Copper indium selenide										
i	0·12 M CuSO$_4$ + TA (pH ~ 3) and 0·08 M In$_2$(SO$_4$)$_3$ (pH ~ 3)	0·05 M Na$_2$SeSO$_3$ (pH ~ 12)	27	Glass	20	40	10	80	0·4	The multilayer CuSe and InSe films were deposited to form CuInSe$_2$. The films were nanocrystalline. The electrical resistivity was found to be of the order of 10^2–10^3 Ω-cm	Pathan (2002), Pathan and Lokhande (2003a)
ii	0·12 M CuSO$_4$ + TA + 0·08 M In$_2$(SO$_4$)$_3$ (pH ~ 3)	0·1M Na$_2$SeSO$_3$ (pH ~ 12)	27	Glass, FTO	20	40	10	120	0·43	The XRD and HRTEM studies showed the films to be nanocrystalline CuInSe$_2$. The films looked smooth and uniform from SEM studies. The electrical resistivity was of the order of 10–100 Ω-cm.	
Ternary telluride thin films											
5.5e	Copper indium telluride										
i	0·12 M CuSO$_4$ (pH ~ 5) and 0·08 M In$_2$ (SO$_4$)$_3$ (pH ~ 5)	0·05 M Na$_2$TeO$_3$	27	Glass	15	50	15	50	0·48	The multilayer CuTe and InTe films were deposited to form CuInTe. The films were nanocrystalline. The electrical resistivity was found to be of the order of 10^3 Ωcm.	Pathan (2002), Pathan and Lokhande (2003a)
ii	0·12 M CuSO$_4$ + 0·08 M In$_2$(SO$_4$)$_3$ (pH ~ 5)	0·1 M Na$_2$TeO$_3$	27	Glass, FTO	15	50	15	90	0·52	The films formed were CuInTe$_2$ with tetragonal crystal structure. The films were nanocrystalline. The electrical resistivity was 10–100 Ωcm.	
5.6	Composite thin films										
5.6a	CdS–Bi$_2$S$_3$										
	0·06 M cadmium acetate (pH ~ 9) and 0·003 M bismuth nitrate (pH ~ 11)	0·1 M Na$_2$S (pH ~ 11) 0·1 M CH$_3$CSNH$_2$ (pH ~ 11)	27	Glass, FTO	15	30	15	30 20	0·14	The deposited material consisted of hexagonal CdS and orthorhombic Bi$_2$S$_3$ i.e. (CdS)$_x$(Bi$_2$S$_3$)$_{1-x}$. The films showed *n*-type electrical conductivity. Photo-electrochemical properties were also discussed.	Ahire *et al* (2001b)
5.6b	Bi$_2$Se$_3$–Sb$_2$Se$_3$										
	0·1 M Bismuth nitrate (pH ~ 8) and 0·2 M potasium antimony nitrate (pH ~ 5)	0·1 M Na$_2$SeSO$_3$ (pH ~ 8·5)	27	Glass, FTO	60	40	60	350	0·185	The films were grown by multilayers of Bi$_2$Se$_3$ and Sb$_2$Se$_3$. The estimated grain size was 50–55 nm and the electrical resistivity was of the order of 10^5 Ω-cm, with *n*-type electrical conductivity.	Sankapal *et al* (2001)

large fluctuations. Its special features like transparency and conductivity dragged it in variety of applications such as energy window, liquid crystal display, solar cells, gas sensors, ultrasonic oscillators, transducers etc (Chopra *et al* 1983; Paque *et al* 1983; Belgit *et al* 1991; Guillemole *et al* 1991; Mazanc *et al* 1991; Olvera *et al* 1993). The electrical resistivity is found to be of the order of 10^8 Ωcm. The deposition of zinc oxide thin films was carried out by many workers (Ristov *et al* 1987; Jim´enez-Gonz´alez and Nair 1995; Tolstobrov and Tolstoi 1995; Jim´enez-Gonz´alez and Su´arez-Parra 1996; Jim´enez-Gonz´alez 1997; Mitra *et al* 1998a,b; Chatterjee *et al* 1999; Lindroos and Leskel¨a 2000).

5.4c *Manganese oxide*: Manganese oxide belongs to VII–VI compound semiconductor material. The optical band gap is ~ 2·6 eV. The films have electrical resistivity between 10^6 and 10^8 Ωcm. Manganese oxide electrodes have promising character of practical use in water electrolysis, photoelectrochemical cells and superconductivity. The deposition of manganese oxide were carried out by Tolstoy *et al* (1997).

5.4d *Cerium oxide*: Cerium oxide belongs to III–VI compound semiconductor material. This compound has an important practical use, as a precursor in the technology of high-temperature superconductors. The deposition of cerium oxide thin film was carried out by Tolstoy and Ehrlich (1997) and Tolstobrov *et al* (2000).

5.5 *Ternary chalcogenide thin films*

5.5a *Copper indium sulphide*: Copper indium sulphide belongs to I–III–VI compound semiconductor materials. It has tetragonal and cubic crystal structures. The films are black in colour. It has a crystal bulk band gap around 1·55 eV, but on polycrystalline thin film the band gap varies between 1·3 and 1·5 eV, which are close to optimum for solar energy conversion. It is a direct band gap semiconductor and it can be obtained in both, *n* or *p* type conductivity. The electrical resistivity is ~ 0·1 to 100 Ω·cm. $CuInS_2$ is a semiconductor that may crystallize both chalcopyrite structures. $CuInS_2$ material is of particular interest for thin film solar cell applications. The deposition of $CuInS_2$ thin films was carried out by Pathan (2002) and Pathan and Lokhande (2003). Figure 8 shows the high-resolution transmission electron micrograph (HRTEM) of $CuInS_2$ thin film. By HRTEM, random orientation of nanoparticles can be clearly seen. Figure 7 shows the 2D and 3D AFMs of $CuInS_2$ thin film. The film appears to be made up of fine particles or nanoparticles. Plot of log *r* against (1000/*T*) for $CuInS_2$ thin film is shown in figure 10.

5.5b *Cadmium zinc sulphide*: Cadmium zinc sulphide belongs to II–II–VI compound semiconductor materials. It has cubic and/or hexagonal crystal structure. The optical band gap and electrical resistivity are of the order of 2·5 to 3·6 eV and 10^4–10^{12} Ωcm, respectively. $Cd_xZn_{1-x}S$ ternary alloy compound are promising materials for a variety of optical devices applications, such as electroluminescent and photoconductor devices and photovoltaic cells. Solid solution of CdZnS thin film can be used in solar cells instead of CdS film, to reduce the mismatch between CdS and Cu_xS. The CdZnS thin films can be used not only with Cu_xS but also with different materials such as CdTe, $CuInSe_2$, $CuGaSe_2$ etc. The deposition of CdZnS thin films was carried out by Nicolau *et al* (1990).

5.5c *Cadmium indium sulphide*: Cadmium indium sulphide belongs to II–III–VI compound semiconductor materials. It has spinel cubic structure. The optical band gap is ~ 2·12 eV and electrical resistivity is of the order of 10^4 Ωcm with *n*-type electrical conductivity. Cadmium indium sulphide is photoactive and has received attention as a prospective material for solid state and PEC solar cells. The thin films of $CdIn_2S_4$ were deposited by Pathan *et al* (2001c).

5.5d *Copper indium selenide*: $CuInSe_2$ belongs to the group of I–III–VI ternary chalcopyrite semiconductor compounds, having a band gap of the order of 1 eV and a very high absorption coefficient near the band edge. It is a direct band gap semiconductor and it can be obtained in both, *n* or *p* type conductivity. $CuInSe_2$ and its solid solutions with $CuInGaSe_2$ and $CuInS_2$ are among the leading candidates for low cost terrestrial photovoltaic devices. The reported conversion efficiency (11·0%) and excellent stability with (Cd, $ZnS/CuInSe_2$) thin film solar cell, makes the ternary thin film polycrystalline semiconductor, $CuInSe_2$, as a strong candidate for photovoltaic devices. The optical properties of such films are very important in view of the intensive interest in the optoelectronic properties. The $CuInSe_2$ thin films were deposited by Pathan (2002) and Pathan and Lokhande (2003a).

5.5e *Copper indium telluride*: Copper indium telluride belongs to I–III–VI compound semiconductor materials. It has tetragonal crystal structure. The films are blackish in colour. The optical band gap is ~ 0·95 eV. Electrical resistivity is of the order of 10–100 Ωcm. It is a direct band gap semiconductor and it can be obtained in both, *n* or *p* type conductivity. The $CuInTe_2$ compound semiconductors exhibit chemical and optical properties which make them promising for photovoltaic devices. $CuInTe_2$ is a direct semiconducting direct band gap ($Eg = 0{\cdot}82$–0·96 eV) material which belongs to ternary Cu family. The deposition was carried out by Pathan (2002) and Pathan and Lokhande (2003).

5.6 *Composite thin films*

5.6a *Cadmium sulphide–bismuth sulphide*: Cadmium sulphide and bismuth sulphide are promising semiconducting materials in the conversion of the solar energy into electrical energy by means of PEC process. However, if each of them is considered separately, it is impossible to fulfil all the desired requirements of the semiconductor to be used because the band gaps of CdS (2·4 eV) and Bi_2S_3 (1·4 eV) do lie close to solar energy spectrum maximum. In this respect, new solar energy materials are needed to consider which of them satisfy the technical properties. It is found that by formation of composite films by combination of two semiconductors we get better results in photoconductivity. The films were deposited by Ahire *et al* (2001b).

5.6b *Bismuth selenide–antimony selenide*: Compound of the column V–B and VI–B elements in the periodic table with chemical formula $MV–B_2NVI–B_3$ basically. These materials cast as semiconductors. Their compounds have been of interest in the study of photoconductivity, photosensitivity and thermoelectric power. The Bi_2Se_3 and Sb_2Se_3 compounds are the members of the above group of materials. The combination of two may give better result in the application of photosensitivity and photoconductivity. The films were deposited by Sankapal *et al* (2001). X-ray diffraction pattern of Bi_2Se_3–Sb_2Se_3 films deposited onto amorphous glass is shown in figure 5b (iii). It was observed that films deposited onto amorphous glass substrate are nanocrystalline consisting of fine grains.

6. Conclusions

In the present review article, we have described the successive ionic layer adsorption and reaction (SILAR) method for the deposition metal (binary, ternary, composite etc) chalcogenide thin films. It is concluded that (i) SILAR method can be used to prepare metal chalcogenide thin films, (ii) SILAR is a cheap method, making the process feasible for commercial application, (iii) wastage of material is avoided as no precipitate is formed during this process, (iv) the materials are stoichiometric and (v) doping of semiconductors, desired type for device formation etc can be achieved.

The optimization of various preparative parameters has been tabulated along with film properties. The film properties are well comparable with the properties obtained by other chemical methods. This shows the wide applicability of SILAR method for deposition of various metal chalcogenides. These chalcogenides are technologically important in device formation based on solar selective coatings, solar cells, photoconductive cells etc where large area is desirable. At the same time, SILAR opens a window for the preparation of nanocrystalline films, which are important for finding new applications.

Abbreviations: Ad, Adsorption time; CBD, chemical bath deposition; Cy, total number of deposition cycles; EN, ethylenediamine; FTO, fluorine doped tin oxide; FM, force modulation microscopy; HH, hydrazine hydrate; ITO, indium doped tin oxide; LFM, lateral force microscopy; PEC, photoelectrochemical; Re, reaction time; Ref, references; Ri, rinsing time; SILAR, successive ionic layer adsorption and reaction; subs, substrate; TA, tartaric acid; TEA, triethanolamine; Temp, deposition temperature; Th, thickness of the film.

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