CHAPTER 1

CBD technique in the preparation of semiconductor thin films for photovoltaic applications – A review

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Reference
1.1 Chemical Bath Deposition (CBD)

As David Smyth-Boyle's homepage\(^\dagger\) puts it, CBD refers to '..... a typical synthesis employing mild conditions.' The technique of Chemical Bath Deposition involves the controlled precipitation of a compound from a solution on a suitable substrate. This technique offers many advantages over the more established vapour phase routes to semiconducting thin films, such as CVD, MBE and spray pyrolysis. In this preparation technique it is possible to control the film thickness and composition by varying the solution pH, temperature and reagent concentration. The ability of CBD to coat large areas in a reproducible and low cost process is one added attraction of this method. The first report of CBD was in 1884 [1] for the preparation of PbS. Today a wide range of chalcogenides (eg. CdS, ZnSe, MnS) and chalcopyrite materials (e.g. CuInS\(_2\) and CuInSe\(_2\)) have been prepared using this method.

The pioneers in this field include Bode et al. at Santa Barbara Research Center, G.A Kitaev et al. at Ural Polytechnic, USSR, Chopra et al. at Indian Institute of Technology, Delhi, and P.K. Nair et al. at Centro de investigation en Energia, Mexico.

1.1.1 Applications of CBD

The use of PbS and PbSe as photodetectors form the first recorded application of chemically deposited semiconductor thin films [2]. This was followed by CdSe photodetectors [3]. Around 1980, the focus of CBD films slowly turned towards solar energy applications. One of the earlier developments towards this was in solar absorber coatings [4]. Application in the field of solar control coating was suggested in 1989 [5]. It has been found that chemical bath deposited PbS and Cu,S thin films offer comparable or superior solar control characteristic as against commercial solar control coatings deposited by much expensive vacuum coating techniques.

\(^\dagger\) http://www.ch.ic.ac.uk/obrien/barton/dsb/dsbcbd.html
CdS and CdSe turned out as probable candidates in the field of photoelectrochemical solar cells [6-9]. Recently, work on chemically deposited CdSe and Sb$_2$S$_3$ films with incorporation of WO$_3$ has shown appreciable conversion efficiency and stability in photoelectrochemical solar cell configuration [10].

It is only 10 years since chemically deposited thin films have found their active role in thin film solar cells. In 1990, a thin layer of CBD CdS thin film was integrated into a structure Mo/CulnSe$_2$/CdS/ZnO producing approximately 11% conversion efficiency [11]. Later improved cell design resulted in record efficiencies greater than 17% [1-18]. Theoretical calculations have shown that the thickness of CdS film should be as small as possible for better cell efficiency. This could be attained easily by CBD technique. The fabrication of heterojunction solar cells using chemically deposited Sb$_2$S$_3$ thin films on p(Si)/p(Ge)/p(InP) wafers has been reported recently [13,14].

P. K. Nair and group have many publications on this simple technique of CBD [15-18]. Lokhande et al. [19] in his review article has mentioned about more than 35 compounds prepared using this technique. All these hint that the number of materials that are deposited by CBD will increase significantly in the coming years.

In the field of CBD, the Photovoltaic laboratory at University of Science and Technology has also contributed significantly. The first CIS/CdS trial thin film solar cell in which both the n- and p-type materials were prepared using CBD technique comes to the credit of the same group (section 1.2.1.h). We have also succeeded in depositing elemental selenium thin films from an acidified bath of sodium selenosulfate. This work is to be published in the forthcoming issue of Thin Solid Film [20]. Moreover, work in the direction of preparation of ternary chalcogenides of CuInSe$_2$ and CuInS$_2$ by diffusing In into the chemically deposited thin film of Cu$_2$Se and Cu$_x$S are in progress.

So to conclude the history of CBD technique- The scope of this technique in the field of photovoltaics is immense. This can form the most ideal technique for the production of large area thin films required for solar energy applications.

1.1.2 Principle of CBD technique

In chemical bath deposition process, precipitation of the solid phase occurs due to the super saturation in the reaction bath. At a given temperature when ionic
product of reactants exceeds the solubility product, precipitation occurs. Where as if
the ionic product is less than the solubility product, then the solid phase produced will
dissolve back to the solution resulting in no net precipitation. This forms the basic
principle behind any chemical deposition process. Or in other words, the principle of
CBD technique is to control the chemical reaction so as to effect the deposition of a
thin film by precipitation.

This deposition technique is mostly used for preparation of metal chalcogenide thin films. In a typical CBD procedure, substrates are immersed in a
solution containing the chalcogenide source, the metal ion and an added base. A
complexing agent is added to control the hydrolysis of the metal ion. The process
depends on the slow release of chalcogenide ions into an alkaline solution in which
the free metal ion is buffered at a low concentration. The free metal ion concentration
is controlled by the formation of complex species according to the general reaction,

\[ M(A)^{2+} \leftrightarrow M^{2+} + A. \]

Here concentration of the free metal ions at a particular temperature is represented by
the relation

\[ \frac{[M^{2+}][A]}{[M(A)^{2+}]} = K_i \] (\( K_i \) being the instability constant of the complex ion). The
instability constant is different for different complexing agents. As the instability
constant increases, more number of ions will be released. The stability of the complex
also depends on temperature and pH of the reaction bath. Increase in temperature of
the solution will make the complex less stable, where as an increase in pH generally
makes it more stable. Thus the concentration of metal ions can be controlled by the
concentration of an appropriate complexing agent and the temperature of the reaction
bath. The common complexing agents needed for certain ions are given in Table
(1.1).

If high concentration of S\(^{2-}\) or Se\(^{2-}\) ions exists locally such that the solubility
product is exceeded, localized spontaneous precipitation of a sulfide or selenide may
occur as the case may be. This situation can be avoided by generating chalcogen ions
slowly and uniformly throughout the volume of the solution. For example, this is
achieved in the case of sulfur by having thiourea in alkaline aqueous solution, so that
the reaction given below proceeds slowly.

\[
(NH_2)_2CS + OH^- \rightarrow CH_2N_2 + N_2 + H_2O + HS^-
\]

\[
HS^- + OH^- \rightarrow H_2O + S^{2-}
\]
Selenide films are obtained by replacing thiourea by selenourea or other derivatives. Selenium ions are generated by dissolving inorganic sodium selenosulphate in an alkaline solution as given by the reaction
\[ \text{Na}_2\text{SeSO}_3 + \text{OH}^- \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{Se}^{2-} \]

<table>
<thead>
<tr>
<th>Elements</th>
<th>Complexing agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>CN⁻, NH₃, Cl⁻</td>
</tr>
<tr>
<td>Cd</td>
<td>CN⁻, NH₃, Cl⁻, C₆H₅O₇⁻, C₄H₄O₆²⁻, EDTA</td>
</tr>
<tr>
<td>Co</td>
<td>CN⁻, NH₃, SCN⁻, C₆H₅O₇⁻, C₄H₄O₆²⁻</td>
</tr>
<tr>
<td>Cu</td>
<td>CN⁻, NH₃, Cl⁻, EDTA</td>
</tr>
<tr>
<td>Hg</td>
<td>CN⁻, NH₃, Cl⁻, EDTA</td>
</tr>
<tr>
<td>Mn</td>
<td>C₂O₄²⁻, C₆H₅O₇⁻, C₄H₄O₆²⁻, EDTA, CN⁻</td>
</tr>
<tr>
<td>Ni</td>
<td>CN⁻, NH₃, SCN⁻, EDTA</td>
</tr>
<tr>
<td>Pb</td>
<td>EDTA, C₆H₅O₇⁻, C₄H₄O₆²⁻, OH⁻</td>
</tr>
<tr>
<td>Sn</td>
<td>C₆H₅O₇⁻, C₄H₄O₆²⁻, OH⁻, C₂O₄²⁻</td>
</tr>
<tr>
<td>Zn</td>
<td>CN⁻, NH₃, C₆H₅O₇⁻, C₄H₄O₆²⁻, EDTA</td>
</tr>
</tbody>
</table>

Table (1.1) Ions and their common complexing agents

1.1.3 Process of thin film deposition

There are three different possibilities for the process of thin film deposition in CBD technique. They are schematically shown in Fig. (1.1). First possibility is the ion-by-ion process in which the ions condense at the reacting surface to form the film. The second is the cluster-by-cluster process in which colloidal particles that are formed in the solution as a result of homogenous reaction gets adsorbed at the substrate surface to form thin layers. Usually both these processes may occur or may interact each other, leading to films in which colloidal material is included in the growing films. The predominance of one mechanism over the other is governed by the extent of heterogeneous and homogeneous nucleation. Heterogeneous nucleation is a result of reaction occurring at the surface of the substrate while homogeneous nucleation is a result of reaction occurring within the bulk of the solution.
1.1.4 Factors influencing the deposition process

The various factors that influence the deposition process in CBD technique are (1) nature and concentration of reactants and complexing agent, (2) temperature, pH and duration of the reaction and (3) nature and spacing of the substrates.

1.(a) Nature of the reactants

Nature of the reactants influences the composition of the products. In the preparation of copper selenide it is observed that when sodium selenosulfate is used as the selenium source, the final phase is usually Cu$_2$Se, while the use of dimethyl selenourea results is CuSe phase [21-23]. The growth kinetics also depends on the nature of reactants. For example, when metal sulfate is employed to deposit metal selenide films using sodium selenosulfate, the rate of deposition decreases and the terminal thickness increases. Here the SO$_4^{2-}$ ions obtained from the metal sulfate reduce the concentration of Se$_2^-$ ions.

1.(b) Concentration of reactants

The deposition rate and terminal thickness initially increases with an increase in the ionic concentration of the reactants. However, at high concentration the precipitation becomes very fast, leading to decrease in film thickness on the substrate.

1.(c) Nature of complexing agent

Nature of complexing agents may influence the final products. For example, when ammonia is used as a complexing agent for the preparation of ZnS thin film, it is found to result in ZnO/Zn(OH)$_2$ phase rather than ZnS. However when two complexants ammonia and hydrazine are used, the oxide and hydroxide phases could be avoided to a great extend [24].

1.(d) Concentration of complexing agent

In a general reaction the metal ion concentration decreases with increasing concentration of the complexing ions. Consequently the rate of reaction and hence precipitation are reduced leading to a larger terminal thickness of the film. Such behaviour has been observed for CdSe, CdS, PbSe and ZnS films.

2.(a) Reaction temperature

Temperature of deposition is another factor that influence the rate of reaction. As temperature increases dissociation of the complex increases. The kinetic energy of
the molecules also increases leading to greater interaction between ions. This will result in increase or decrease of terminal thickness, depending on the extent of super saturation of the solution.

2.(b) Reaction pH

When the pH value of the reaction bath increases, the metal complex usually becomes more stable, reducing the availability of free metal ions. This will decrease the reaction rate resulting in higher terminal thickness.

Recently there was a report by Paul O’ Brien [25], on a novel approach to the deposition of CdS by CBD. He succeeded in depositing CdS from an acidic bath for the first time. It was observed that the film properties were very much different in the case of such films when compared with that of films deposited from alkaline bath.

2.(c) Duration of reaction

The dependence of film thickness on the duration of deposition (all the other factors remaining the same) has been studied in detail for different semiconductor thin films obtained by CBD technique [15]. The results are summarised in Fig.[1.2]. In general, the growth of good quality semiconductor thin films proceeds at a slow rate. This technique of CBD is ideally suited for producing uniform films with thickness in the 0.05-0.3 μm range in most cases and rarely to an extend of few microns.

3.(a) Nature of substrates

This factor plays a major role in the reaction kinetics and in the adhesion of the deposited film. Hence cleaning of substrate surface form the first important step in the thin film deposition procedure.

Higher deposition rates and terminal thickness are observed for those substrates whose lattices and lattice parameters match well with those of the deposited material. During deposition of PbSe thin films under similar conditions, higher rates and thickness have been observed on Ge rather than on Si because of better matching of the lattice parameters of PbSe with those of Ge [26].

On a presensitised substrate surface, no incubation period for nucleation is observed since nucleation centers already exist on the substrate. Also when the substrates are suspended in the container before forming the complex in the solution, film thickness increases in a manner similar to that of the sensitised surface, there by
Fig. (1.1) Representation of various processes of thin film deposition in CBD technique

Fig. (1.2) Dependence of film thickness on duration of deposition
showing that the nuclei for the formation of the film are provided by the solution itself.

3.(b) Spacing of substrates

Recently Arias- Carbajal et al. [27] have studied the film thickness as a function of separation between substrates in batch production. It was observed that film thickness reach an asymptotic maximum with increase in substrate separation. This behaviour is explained on the basis of the existence of a critical layer of solution near the substrate, within which the relevant ionic species have a higher probability of interacting with the thin film layer that contribute to precipitate formation. The critical layer depends on the solution composition, the temperature of the bath, as well as the duration of deposition. In the case of CdS thin film, this critical layer is found to extend from 0.5 to 2.5 mm from the substrate surface, depending on the deposition conditions.

The above mentioned influencing factors do not actually affect the chemical reaction individually, but the final result is due to the cumulative effect of interdependence of all these factors. K. L. Chopra and S. R Das in ‘Thin Film Solar Cells’ have represented the influence of few of the above parameters on the thickness of the deposited film as experimental graphs. [26].

1.1.5 Mathematical model for CBD growth

P. K. Nair et al. has worked out a mathematical model simulating the growth of compound semiconductor thin films via. chemical bath deposition [28]. This model can be used to simulate the growth curve of the CBD thin films for large area coatings as a function of the initial concentration, temperature and duration of deposition. Development of this model was based on the experimental growth curve of thin films of different materials grown in this method. The general characteristics of the different stages in CBD growth process were classified as:

1 The existence of an induction period called the nucleation or incubation period, during which the various chemical equilibria are established in the bath and an initial monolayer of the metal chalcogenide is formed on the substrate.
The initial monolayer of the metal chalcogenide formed on the substrate acts as a catalytic surface for the condensation of the metal ions and chalcogenide ions resulting in the film growth. This is called the growth phase.

Film growth assumes a maximum rate at a certain time, depending on the bath parameters and finally reaches a terminal phase at which the film ceases to grow.

A decrease in the duration of the induction period with increase in the temperature as well as with the concentration of ions in the bath.

An optimum temperature-concentration combination to obtain maximum film thickness for a given duration of deposition.

In this technique, the metal ions are complexed with ligands and depending on their instability constant they will slowly dissociate releasing free metal ions. This forms the main rate determining step. Hence first order reaction rate kinetics is applied to the dynamics involved in CBD process.

\[
\frac{dC(t)}{dt} = -kC(t) \quad \text{where } C(t) \text{ is the unreacted metal ion concentration at time } t \text{ resulting from an initial concentration } C_i.
\]

\[
C(t) = C_i \exp(-kt) \quad \text{where } k = A \exp(-E_a/RT)
\]

(A is the Arrhenius constant, \(E_a\) the activation energy, \(R\) the universal gas constant and \(T\) the temperature). The used up concentration \(C_u(t)\) of the metal ions can be expressed in the form of Avrami equation

\[
C_u(t) = C_i \left[1 - \exp(-kt)\right]
\]

Based on the theory developed with this idea and the concepts of geometric factor and induction factor, the growth curve for CdS thin film was simulated. This was found to be in good agreement with the experimental curve.

The other important experimental observations that were reaffirmed through this modal include,

(i) It is necessary to combine a relatively high initial metal ion concentration with a relatively low temperature of deposition for getting films of thickness greater than 0.5 \(\mu\)m by single dip.

(ii) If the objective is to deposit a very thin film of typically 0.05 \(\mu\)m, a very dilute bath and a relatively high deposition temperature is appropriate.
1.1.6 Quantum confinement effect

Thin films of several materials deposited using chemical bath possess a nanocrystalline structure [29]. Small crystal size leads to quantum size effect and a blue shift is observed in the optical spectra. In the case of CdSe, it is observed that there is a certain critical ratio between the complexing agent and Cd concentration in the bath used for preparation of the film, below which there is a pronounced blue shift [30]. This observation was correlated with decrease in crystal size.

In the case of a polycrystalline semiconductor with crystalline grain width L, the enhancement of band gap \((E_{g})_{pc}\), as compared to that of a bulk semiconductor crystal, can be represented as [31].

\[
(E_{g})_{pc} = (E_{g})_{bulk} + \frac{\hbar^2}{2\pi^2} \left( \frac{m_{e}^{-1} + m_{h}^{-1}}{L^2} \right) - \frac{1.8}{\xi L}
\]

where \(m_{h}\) and \(m_{e}\) are the effective masses for hole and electron respectively. The last term represents 'screening term' in a medium of permittivity \(\xi\). \((E_{g})_{pc}\) generally approaches \((E_{g})_{bulk}\) for \(L > 50\) nm, but takes values considerably higher than the bulk value for \(L < 5\) nm. For example, in the case of CBD-CdSe films, with grain sizes < 5 nm, optical band gap goes up by \(-0.7\) eV above the bulk value (1.74 eV) [29]. Annealing of as-prepared films improves the crystallinity and hence the discrepancy in band gap will be reduced [32].

1.1.7 Photoresponse of CBD films

A comparative study on photocurrent response of a number of chemically deposited thin films has been reported, Fig (1.3) [15]. Except for CdS, the films do not exhibit large photocurrent. Most of the films were highly resistive in the dark and their electrical conductivities in dark varied in the range \(10^{-8}\) to \(10^{-6}\) Ω\(^{-1}\)cm\(^{-1}\). Exceptions were CuS and Cu\(_{2}\)\_Se thin films, where conductivities were in the range \(10^{4}\) - \(10^{3}\) Ω\(^{-1}\)cm\(^{-1}\). Such high conductivities were reported to arise from copper deficiency in these films, which make them p-type [33]. This is also responsible for the large free carrier absorption in these films in the IR region.

Air annealing is found to have significant influence in the photoresponse of some of the chemically deposited semiconductor films. It is reported that though the CdSe thin films possess very poor photosensitivity, annealing in air makes the film highly photoconductive. This is due to the combined effect of grain size growth and
chemisorption of oxygen [34,35]. Fig.(1.4) represents this effect figuratively, where photosensitivity \( S \) is defined as \( S = \frac{(I_{ph} - I_d)}{I_d} \) (\( I_{ph} \) and \( I_d \) are the photocurrent and dark current respectively).

On the other hand photoconductivity of CdS is found to degrade under the same annealing process, [Fig.1.5]. The photosensitivity of the as-prepared films gets lowered by 4 to 5 orders due to annealing at 300-400°C. Annealing at high temperatures improves the dark conductivity drastically [36]. This is due to the formation of a top layer of CdO [37].

1.1.8 Advantages and disadvantages of CBD technique

Advantages

1) **CBD is a simple and low cost technique:**

Of all the thin film deposition techniques, CBD is the simplest as no elaborate arrangement is required. It can be as simple as given in Fig.[1.6], with a beaker containing the reaction bath and glass slides dipped in it. It is to be specifically noted that the deposition is usually carried out at atmospheric pressure and at relatively low temperature.

The above mentioned reasons along with the fact that high purity chemicals is not an essential requirement, makes this a low cost technique. In this method there is very little chance of incorporation of impurities from the reaction bath on to the deposited thin films. Only if the impurities present in the bath are capable of forming insoluble compounds under the existing conditions of deposition, there is chance of incorporation into the film. This will happen only if the ionic product of the impurity species is greater than its solubility product. However chances of this are rare, as the impurity concentrations will be usually less than 2%.

2) **Multicomponent films can be prepared**

With CBD technique it is possible to deposit multicomponent chalcogenide thin films over a wide range of stoichiometry. Some of the ternary alloys prepared using this method are given in Table (1.2) [26].

Alloys of chalcogenide films are prepared by reacting sodium selenosulfate or thiourea with a mixture of different complexed metal ions. If two non-interfering and independent complexing agents (say A and B) are used for complexing two
Fig.(1.3) Photocurrent response of various semiconductor thin films prepared by chemical bath deposition technique.

Fig.(1.4) Variation in the photosensitivity of the films produced by annealing of a CdSe film (~150nm) in air for 1 h each at different temperature.
Fig.(1.5) Variation of photosensitivity of CdS film with annealing in air at different temperatures for 1 hr
Fig. (1.6) Set up for chemical bath deposition of thin films
cations (say M and M'), then the ions dissociate in an aqueous solution to give free metal ions according to the reactions

\[ M(\text{A})_{n}^{2+} \leftrightarrow M^{2+} + n\text{A} \]

and \[ M'(\text{B})_{m}^{2+} \leftrightarrow M'^{2+} + m\text{B} \]

The stoichiometry of the as-deposited film depends on the initial salt concentration, complexing salt concentration and temperature of the bath. An alternative technique to vary the composition is to change the concentration of the complexing agents without altering the ratio of the salt concentrations. For example, the composition of Cd_{1-x}Pb_{x}Se films could be varied by adding different amounts of NH_{4}Cl solution to the reaction mixture [26].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb_{1-x}Hg_{x}S</td>
<td>(0 \leq x \leq 0.33)</td>
</tr>
<tr>
<td>Pb_{1-x}Hg_{x}Se</td>
<td>(0 \leq x \leq 0.35)</td>
</tr>
<tr>
<td>Cd_{1-x}Hg_{x}S</td>
<td>(0 \leq x \leq 1.30)</td>
</tr>
<tr>
<td>Cd_{1-x}Hg_{x}Se</td>
<td>(0 \leq x \leq 0.15)</td>
</tr>
<tr>
<td>Cd_{1-x}Zn_{x}S</td>
<td>(0 \leq x \leq 1)</td>
</tr>
<tr>
<td>Cd_{1-x}Pb_{x}Se</td>
<td>(0 \leq x \leq 1)</td>
</tr>
<tr>
<td>CdSe_{1-x}S_{x}</td>
<td>(0 \leq x \leq 1)</td>
</tr>
<tr>
<td>PbSe_{1-x}S_{x}</td>
<td>(0 \leq x \leq 1)</td>
</tr>
</tbody>
</table>

Table (1.2) Few alloys prepared using CBD technique

3) Inteutype conversion possible by easy methods

Many of the chemical bath deposited intrinsic semiconductors can be converted to n-type or p-type by easy and simple methods. For example, immersion of intrinsic CBD-CdS thin film in a dilute solution (0.05 M) of HgCl₂ for a few minutes and annealing in air at 200°C, produces n-type conductivity of \(~1\ \Omega^{-1}\text{cm}^{-1}\) [36]. Similar results are reported for CdSe also [38]. This result is attributed to chlorine incorporation in the film. The main drawback of this conversion is loss of conductivity at high annealing temperatures. Recently another method was suggested for the conversion of CdS and CdSe to n-type [39-41]. This was based on evaporation
of a 20 nm thick indium layer on to the film surface and annealing at 300-350°C. This resulted in n type films of low resistance and high stability.

The conversion of CBD-CdS thin films to p-type by topoaxial reaction in copper chloride solution is well known. The incorporation of copper ions in CBD-CdSe thin films by immersion in a dilute solution of CuCl₂ (0.005 M) result in p-type conductivity with the reduction in sheet resistance from \( 10^{12} \Omega/\square \) to \( 10^{5} \Omega/\square \) \[15\]. A similar case with ZnSe is also reported \[42\]. In ZnS-CuS or PbS-CuS multilayers, thermally stable p-type films of low sheet resistance can be prepared by interfacial diffusion of metal ions \[16\].

4) **It is a safe procedure with minimum environmental hazards**

Safety of this technique arises from two angles: 1) Due to the simplicity of the procedure which avoids sophisticated setup or high temperature and pressure. 2) It does not involve reactants in the vapour phase. For example, while the usual selenisation process involves H₂Se or Se vapour, they can be avoided in CBD processes. It is well known that toxicity hazards associated with lead, cadmium, mercury, selenium, etc. are severe when inhaled. An analysis on the toxicity hazards in the production of chemically deposited PbS thin films is given in Ref.\[43\], where it was established that the chemical bath technique does not entail the usual health hazards associated with lead pollution.

5) **Suitable for large area deposition**

Large area deposition is necessary for commercial purpose. This is possible with in this technique by carefully laying down the substrate on a shallow tray containing the deposition bath. The substrate surface should be kept at a height of 5 mm from the bottom of the tray with the help of spacers. In such an arrangement the film deposited at the bottom surface is found to be of better quality. Coatings on glass sheets of 60x60 cm² are usually prepared from 2000 ml of solution using the above arrangement \[15\]. This technique can be used for uniform film coating on substrates of any desired shape and form by suitably choosing the bath container.
6) **Reproducibility is high**

Once all the bath parameters that influence the deposition of thin film are standardised, this technique can give good reproducibility especially in the case of binary compounds.

7) **Wastage can be minimized**

Precipitates are unavoidable in CBD technique. However, in large-scale deposition, precipitate can be filtered out and reacted with acids or other suitable reagents to retrieve the starting materials for deposition. In many cases the precipitate may be rinsed well, dried and stored to serve as precursor for other deposition techniques.

For example, some precipitates can be used for screen-printing or production of composite coatings. Screen-printing has been successfully used in the production of CdSe-CdTe solar cells [44]. This process involves the precipitation of a paste containing the semiconductor pigment, a flux material that will fuse at a temperature much below the melting point of the pigment and a binder usually ethylene glycol or propylene glycol. This paste is printed on suitable substrate using a silk screen or polyester screen, dried for a few hours at 50-80°C and then sintered at a temperature higher than the melting point of the flux.

The precipitate produced in the chemical deposition bath is usually stoichiometric. The purity of such precipitate will be superior to that of the starting chemicals in the bath as the chances of incorporation of impurity is very less in this deposition technique. Thus the precipitate can serve as a relatively pure source of semiconductor material for vapour phase deposition [45].

**Disadvantages**

1. It is not easy to dope the intrinsic semiconductor thin films with external dopants at the time of film formation. This is due to the fact that slight concentrations of dopants included in the reaction bath will not be incorporated to the film unless the condition for precipitation (i.e. ionic product > solubility product) for that particular dopant is satisfied.

2. When used for the deposition of ternary and other multicomponent compounds, the control of stoichiometry will be difficult. In order to ensure the reproducibility of the process a precise knowledge of the effect of various parameters on the growth medium should be thoroughly understood.
3. Selection of substrate is restricted in CBD as there is possibility of reaction of substrate with the reaction mixture. Hence inert materials such as glass or SnO$_2$/ITO coated glass or inert metal surfaces are required.

4. Deposition of multilayers by CBD technique has to be done carefully. Or in other words, order of deposition of multilayers is to be selected. This is due to the possibility of reaction of the initially deposited layer with the solution bath meant for depositing the second layer. For example, CulnSe$_2$ cannot be deposited over CdS to form a multiplayer since CdS when dipped in a copper containing solution gets partially converted to Cu$_x$S.

5. This technique cannot be used to deposit very thick layer of materials. The maximum thickness attainable in a single dip is more or less fixed. Hence repeated dipping cannot lead to thickness greater than few microns. Moreover, in repeated dipping the chances of pealing off the film is high.

1.2 Various semiconducting thin films prepared by CBD technique for use in photovoltaic applications

The number of semiconducting materials that are deposited by this simple technique of CBD is increasing at a rapid rate. In this review a list of materials that finds application in the field of photovoltaics are included. Neither the list nor the cited references is complete or exhaustive. In the following section an attempt is made to introduce a few of these materials, with special emphasis on CdS and CulnSe$_2$.

1.2.1 Cadmium sulfide (CdS)

As far as photovoltaic is considered, CdS is the most successful material prepared using CBD technique. This is an extensively studied material with its direct band gap, high absorption coefficient, good electronic affinity and effective ohmic contact [46]. Growth of CdS is usually columnar and perpendicular to the substrate surface [47]. This means that grain boundaries parallel to the junction that impedes the flow of photogenerated carriers are few. This material with its high conversion efficiency and stability has proved to be a good window material in solar cells [48]. Though various deposition techniques such as sputtering [49], spray pyrolysis [50],
vacuum evaporation [51] electrodeposition [52], screen printing [53] and molecular beam epitaxy [54] have been reported for the preparation of CdS, CBD technique has attracted much attention as a simple and promising one to obtain device quality films [55-57].

Even within the field of CBD-CdS, a comparative study of properties is impossible as no two preparation conditions coincide. For example, in the list of preparations given below, the cadmium salt can be seen to vary from sulfate, chloride, acetate, iodide and so on, leave alone the variations in deposition conditions like temperature, pH, duration of deposition, etc. Here an attempt is made to mention some of the gradual progresses on CBD films of this material, with more emphasis on recent works.

\[ \text{a) Photoconductive CdS by CBD process} \]

In 1977 N. R. Pavaskar \textit{et al.} [36] reported a detailed study on photoconductivity in CBD CdS films. He standardised the conditions under which these films could be produced with a high degree of reproducibility with respect to thickness, structure and electrical behaviour. The preparation procedure was as follows: 10 ml of 1 M cadmium sulfate solution and 50 ml of 2 M ammonia solution were mixed to form a complexed compound. To this solution, 10 ml of 1 M thiourea was added. The reaction bath was heated to 80-90°C for 30 min. A pre-cleaned pair of substrate was kept rotating approximately 2.5 cm below the surface of the solution. The films formed were washed in distilled water and preserved in dark desiccator.

\[ \text{b) Growth kinetics} \]

K. L. Chopra \textit{et al.} [58] revealed the growth kinetics of chemical deposition of CdS film from alkaline solution of cadmium acetate, in the year 1980. The kinetics was studied with respect to temperature of deposition and the relative concentrations of the various reactants in the solution. It was established that the growth of the film takes place either by ion-by-ion condensation of Cd^{2+} and S^{2-} ions or by adsorption of colloidal particles of CdS formed in the solution, depending on the various deposition parameters and the method of preparation. The former process of growth result in thin, hard, adherent and highly reflecting films. The same group also proposed a model for growth mechanism.
c) Preparation of device quality CdS films

T. L. Chu *et al.* in the year 1992, deposited device quality CdS film on glass and on SnO$_2$:F/glass substrates from an aqueous solution containing cadmium acetate, ammonia, ammonium acetate and thiourea [59]. Well cleaned SnO$_2$:F/glass substrates were vertically suspended in an aqueous mixture of CdAc$_2$ (10$^{-3}$ M), NH$_4$Ac (0.02 M), NH$_4$OH (0.4 M) and (NH$_2$)$_2$CS (5x10$^{-3}$M) at 85°C under constant stirring. This solution had a pH around 9.1. The reaction started within 10-15 min and was complete in about an hour. The average deposition rate of CdS on SnO$_2$/glass substrate was 20-30 Å/min.

The expected reactions were as follows

\[
\begin{align*}
&NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \\
&Cd^{2+} + 2 OH^- \leftrightarrow Cd(OH)_2 \\
&Cd^{2+} + 4 NH_3 \leftrightarrow Cd(NH_3)_4^{2+} \\
&(NH_2)_2 CS + 2 OH^- \leftrightarrow S^{2-} + 2 H_2O + H_2CN_2 \\
&Cd^{2+} + S^{2-} \leftrightarrow CdS
\end{align*}
\]

d) Conversion to n-type by boron doping

Boron doping was tried by adding Boric acid to the above mentioned reaction mixture [59]. Boron atoms were expected to occupy Cd sites in CdS to serve as donors. Studies were done by varying the molar ratio of BO$_3^{2-}$/Cd$^{2+}$ in the solution in the range 10$^{-5}$ to 10$^{-2}$. This doping made CdS n-type and it was found to have a pronounced effect on the dark conductivity. A minimum in dark resistivity was observed at a BO$_3^{2-}$/Cd$^{2+}$ ratio of 0.001. With further increase in boron concentration, the dark resistivity was found to increase and it finally approached the value for undoped film (around 2x10$^4$ Ωcm). However, the illuminated resistivity of boron doped CdS films deposited at large BO$_3^{2-}$/Cd$^{2+}$ ratios was found to be independent of the boron concentration. From the photoconductivity study of these films it was observed that the incorporation of boron into CdS films increases the time constant appreciably indicating the formation of slow states in the band gap.

e) Conversion to n-type by indium diffusion

Boron doping in CBD-CdS reduced the optical band gap of the as-prepared film. Hence in 1996, P. J. George *et al.* suggested a successful method of indium
diffusion to make CdS n-type and that too without tempering the large band gap of the material [60]. As-prepared CdS thin films were deposited at 80°C for 4 hrs from a chemical bath containing citratocadmium ions and thiourea. An indium layer of 10-40 nm thickness was evaporated on to the CdS film surface that was thermally diffused by heating the sample in air at 250°- 350°C for 1-4 hrs. XPS analysis revealed the diffusion of indium into the CdS film leading to the conversion of chemically deposited intrinsic CdS thin film into n-type with conductivity upto 50 Ω-¹ cm⁻¹. Optical transmittance spectra of these films indicated that the band gap was still > 2.5 eV. This has opened up the scope for using such n-type CdS films directly as a window layer in heterojunction solar cells.

f) CdS deposition from acidic bath

CdS deposition is always associated with baths that are alkaline [61]. However, Paul O'Brien et al. have very recently (1999) reported for the first time that CdS can be deposited from acidic bath containing thioacetamide [62]. CdS thin film was grown on pre-cleaned tin oxide glass substrates from solution containing cadmium salt (chloride 0.02 mol/dm³), urea (0.5 mol/dm³) and thioacetamide (0.2-0.02 mol/dm³), to obtain a solution (100 cm³) of final pH 5.5-4.9. The temperature of deposition was around 75°C and occasional stirring was given.

The adherence of the film was good, but they did not resemble in morphology or properties to the alkaline bath CdS. Air annealing improved the crystallinity of this hexagonal phase and it also induced the migration of chloride ions to the surface region. No evidence of oxidation was observed on air annealing. These results have opened up the possibility of developing ternary films of (CdZn)S under acidic conditions.

g) Modification of CBD apparatus

In the year 2000, G. Sasikala et al. [63] has suggested a modified set up for CBD deposition of CdS. This modification is in order to obtain a precise control over the pH of the reaction mixture. The vital role of pH on the quality of the CBD–CdS films were also revealed with this modified apparatus, Fig.[1.7]. Here the substrate suspended from the sample holder can be rotated at a constant speed so as to ensure homogenous heat transfer to the substrate from the hot reaction bath. A reservoir
arrangement was made for simultaneous addition of thiourea into the bath during the
growth process. A pinch cork was provided to adjust the rate of flow. The other
reactant was cadmium chloride complexed with ammonia. Temperature of deposition
was maintained at (0°C) with the help of oil bath. pH of the reaction bath will
decrease slowly due to evaporation of NH₃ gas. In order to avoid this, the vessel was
provided with mercury liquid seal for the stirrer. Main upper portion of the vessel was
arranged to be exposed to atmosphere in order to help ammonia vapour to condense
and fall back to the deposition solution. To take care of high pressure, a safety valve
was also provided.

h) CBD –CdS based solar cells

**CdS/CdTe cell: (1992)**

T. L. Chu et al. reported an n-CdS/p-CdTe solar cell where the CdS layer
was prepared using chemical deposition [59]. On SnO₂:F/glass substrate device
quality CdS films of thickness 600-1000Å was deposited as mentioned earlier in
section (c). It was converted to n-type through boron doping (as mentioned in section
(d)). On to such a layer, p-CdTe film was deposited using close-spaced sublimation
(CSS) technique. Substrate (CdS/SnO₂:F/glass) and the polycrystalline CdTe source
were separated by about 0.2 cm. Source materials and substrate were maintained at
about 700°C and 600°C respectively. The deposited film was 4 to 5 μm thick. Devices
of about 1cm² area were isolated. The study conducted at NREL revealed that such
solar cells could give efficiency higher than 14.5% under global AM 1.5 conditions.

**CdS/CIS cell: (1996)**

Hai-Ning Cui and Shi-Quan Xi in 1996 reported the test trial of ITO/dip-
CdS/CIS/Mo/glass structured cell. This cell with chemically deposited CdS acting as
widow layer and CIS (CuInSe₂) acting as absorber layer showed considerably high
efficiency [64]. Here chemically deposited CdS was prepared as follows
Solution 1: CdCl₂ (0.01 M), NH₄Cl (0.039 M), NH₂OH (0.76 M)
Solution 2: Thiourea (0.17 M); NH₂Cl (0.039 M); NH₂OH (0.76 M)
Equal volumes of solutions 1 and 2 were mixed at 50°C and placed in the deposition
beaker in which cleaned glass slides were kept vertically. This beaker was placed in a
water bath held at 73°C. pH value of combined solution was approximately 11.
During cell construction, in order to increase the optical transmission range of the window material, only a very thin resistive layer of the CdS was used. On this a transparent conducting layer of ITO was deposited using rf sputtering. This double layer formed a good window region for the solar cell.

Recently, a CBD-CdS/CBD-CIS cell was reported and the details of this are included under the following section ‘All-CBD cell’.

**CdS/CIGS cells: (1998)**

Y. Hashimoto *et al.* [65] fabricated a solar cell with an active area of 0.48 cm², with a structure MgF₂/ITO/ZnO/CdS/CIGSIMo/glass. The high quality CIGS (copper indium gallium selenide) film was deposited on Mo coated soda lime glass by applying the composition monitoring system to the 3-stage process. Stoichiometric CdS layer of thickness 100Å was deposited on the CIGS layer by CBD technique. The chemicals used for this include equal amount of 0.0014 M CdI₂, NH₃ and 0.14 M CdI₂, NH₃ and 0.14 M thiourea solution. The deposition was carried out in a solution of pH 11.8, at a temperature of 70°C and the duration of deposition was 20 min. The ZnO layer with thickness of 0.2 μm and the ITO layer with thickness of 0.1 μm were deposited by RF magnetron sputtering. The MgF₂ antireflection layer with thickness of 0.12 μm was deposited by electron beam evaporation. The device had a high conversion efficiency of 17% (V_{oc} = 0.65 V, J_{sc}=35.1 mA/cm², FF = 0.747). This result indicates that the performance of the solar cell becomes appreciable on improving the stoichiometry of the CdS layer by CBD technique.

**All – CBD Cell:**

The first report of ‘All-CBD cell’ i.e. CBD-CdS/CBD-CIS cell was from the Photovoltaic laboratory, Dept. of Physics, Cochin University of Science and Technology [66]. The details of cell fabrication is as given below:

A SnO₂:F/glass substrate was dipped in a reaction mixture containing aqueous solutions of copper citrate (7.5 ml, 0.2 M), indium citrate (25 ml, 0.2 M) and sodium selenosulphate (20 ml, 0.1 M). Deposition was carried out at room temperature at a pH of 6.5, under stirring. For a deposition time of 1hr, a thickness ~ 120 nm was obtained. For higher film thickness, repeated deposition was done.
As a next step CdS was deposited on this by CBD technique itself. A reaction bath containing cadmium chloride (CdCl₂), triethanol amine, thiourea and ammonium hydroxide was used. The temperature was kept controlled at 90°C and pH at ~10.5. Film of thickness ~ 600 nm was obtained in 30 min time.

These samples were then annealed in air at 200°C for 7 hrs to improve and stabilise the characteristics. Then the top CdS layer was given a chemical treatment by dipping the sample in hot (50°C) stannic chloride solution (0.5 M) for few seconds and drying at 100°C for 5 min. This was done to reduce the series resistance of the cell. The device fabrication was completed with deposition of a top electrode. The electrode was vacuum evaporated indium in the form of a grid. Then the sample was annealed in a low vacuum of 10⁻¹ Torr at a temperature of 150°C for 1 hr. The total area of the film deposited was 5x1.25 cm². It was divided into small cells of area 0.1cm². Each cell was then tested for its photovoltaic activity.

The schematic diagram of CBD-CuInSe₂/CBD-CdS thin film solar cell is shown in Fig.[1.8] [67]. The cell parameters obtained for the best cell were, $V_{oc} = 365$ mV, $J_{sc} = 12$ mA/cm², FF= 61% and $\eta=3.1\%$ under an illumination of 85 mW/cm² on cell of active area 0.1 cm². The J-V and C-V characteristics and the spectral response were also studied.

### 1.2.2 Cadmium selenide (CdSe)

CdSe thin films with a direct band gap of 1.7 eV and n-type conduction are of great relevance in photovoltaic systems [68]. A recent report of p-type conduction in this material prepared by molecular beam epitaxy (MBE) technique has enhanced its scope [69]. Highly stoichiometric CdSe films are prepared by hot-wall epitaxy, vacuum evaporation and MBE [70,71]. Chemical techniques like spray pyrolysis, screen-printing, electrodeposition and evaporation of the residual precipitate from chemical bath deposition [72-75] are also reported. But a major problem with this polycrystalline film is the considerable reduction in photo response due to the grain boundary defects. A report that appeared this year on the success of laser annealing has given rays of hope for betterment [76].

Based on chemical kinetics it has been found that initiation of CdSe film formation will be possible by CBD technique only in the region of existence of hydroxide [77]. Nair and Nair has suggested the following preparation procedure
Fig. (1.7) Modified chemical bath deposition set up

Fig. (1.8) Schematic diagram of the CuInSe₂/ CdS 'All-CBD' solar cell structure
[34,35], 30 ml of 0.1 M Cd(NO$_3$)$_2$ 4H$_2$O, 12 ml of 1 M sodium citrate, 1.2 ml of 30% (~ 15M) NH$_4$OH and 0.4 g of N,N-dimethyl selenourea dissolved in 30 ml of freshly prepared 0.01 M Na$_2$SO$_3$ is mixed and the volume is made upto 100 ml by addition of water. Thin film deposited from this reaction bath at room temperature after a duration of 24 hrs, is found to be smooth and uniform.

1.2.3 Copper sulfide (Cu$_x$S)

Ever since the discovery of photovoltaic effect in CdS/Cu$_x$S structure in mid fifties, there has been wide spread interest in Cu$_x$S thin films. Various methods such as evaporation, reactive sputtering and improved topoaxial reaction has been tried to obtain Cu$_x$S films with $x \approx 1.997$ as required for solar cell applications [18]. In recent years this material is pursued for its solar control application also [5,8].

Many researchers have reported on chemical bath deposition of Cu$_x$S. Fatas et al. [78] mixed 1 M CuSO$_4$, 1 M sodium acetate and 7.4 M TEA solution and then added 1 M thiourea in alkaline medium. They reported an optical band gap of 2.58 eV and resistivity of the order of $3 \times 10^3 \Omega$cm. A. J. Varkey [79] has reported Cu$_x$S deposition using EDTA as a complexing agent in a bath comprising of CuCl, NaCl and hydroxylamine hydrochloride solutions. In 1993, Gadave et al. [80] did this in a different way. An aqueous solution of 15 ml 0.1 M CuSO$_4$ and 15 ml 1 M sodium thiosulfate was mixed and clean glass slides were introduced in this reaction bath of pH 0.5 for ~ 40 min. The temperature of deposition was 60°C. This resulted in Cu$_x$S films of band gap 2.4 eV and electrical resistivity of the order of $10^4 \Omega$cm.

1.2.4 Antimony sulfide (Sb$_2$S$_3$)

Sb$_2$S$_3$ thin films have been successfully used in schottky barrier solar cells (Pt-Sb$_2$S$_3$) [81] and in hetero junction solar cells (n-Sb$_2$S$_3$/p-Ge) [14] with conversion efficiencies of 5.5% and 7.3% respectively. This material is usually prepared by vacuum evaporation technique [82] and chemical bath deposition technique [14,83,81]. Depending on the deposition process the films may show n or p type conduction [84,85].

For the deposition of antimony sulfide thin films by chemical bath method, Mandal and Mondal [83] used a solution containing potassium antimony tartarate, triethanol amine, aqueous ammonia and thioacetamide. Later, Savadogo and Mandal
[86] showed that addition of a small quantity of silicotungstic acid in the bath yields films with enhanced photoconductivity with WO$_3$ incorporated in them. Grozdanov [87] reported deposition of Sb$_2$S$_3$ films from a bath consisting a solution of SbCl$_3$ (3.5 to 4 g) dissolved in glacial acetic acid (7 ml), 1 M sodium thiosulfate (100 ml) and cold (10-15°C) distilled water (400 to 500 ml). Thin films of thickness up to 1.3 µm were obtained from this bath after 24 hrs of deposition. In 1998, Nair et al. [85] did this in a slightly different way. In a 100 ml beaker, 650 mg of Sb$_2$S$_3$ was dissolved in 2.5 ml of acetone. 25 ml of 1 M sodium thiosulfate at 10°C was added to this and it was followed by the addition of 70 ml deionised cold water. The deposition was carried out at 10°C. Annealing of these as-prepared films at 250°C in nitrogen atmosphere improved the crystallinity, decreased the band gap from 2 eV to 1.7 eV and increased the photosensitivity.

1.2.5 Zinc oxide (ZnO)

Zinc oxide can be used as a transparent electrode material in photovoltaic cells because of its good material properties [88]. Recently this material has evolved as a suitable buffer layer on p-CulnS$_2$, so as to replace the CdS layer. ZnO layer with its band gap of 3.3 eV is found to improve the light transmission in the blue wavelength region. It can be a substitute for CdS layer, thus avoiding the toxic cadmium. There are various deposition techniques for this material [89].

Paul O'Brien [89] deposited ZnO films by CBD. The reaction bath consisted of 0.0188 M Zn and 0.042 M ethylenediamine. The starting pH was made up to 10.5-11 by addition of NaOH. The film grown on clean glass substrates dipped in this reaction bath was uniform and adherent.

Recently, Ennaoui et al. [90] deposited CBD-ZnO by two other procedures. In the first method the substrates were immersed in the beaker containing reaction mixture of dilute tetraamine zinc at 65°C. The second method was SILAR (Successive Ionic Layer Adsorption and Reaction) which consisted of three main steps: (i) specific adsorption of zinc amine solution by substrate immersion in a solution containing Zn(NH$_3$)$_4^{2+}$ at room temperature (ii) introduction of the substrate in hot water at 95°C (iii) water rinsing in order to remove loose ZnO particles before starting a second cycle. A ZnO/CuInS$_2$ junction was fabricated with this CBD-ZnO layer.
In order to compare the performance of this ZnO/CuInS$_2$ junction with that of the standard CdS/CuInS$_2$ solar cell, both junction were prepared and the device properties were measured under AM 1.5 solar spectrum. The output characteristics of the cells and corresponding spectral quantum efficiencies are shown in Fig.[1.9-a,b]. Due to the higher band gap of the ZnO layer, an enhanced response in the short wavelength of the spectrum was observed. However this cell had only a low efficiency of around 4%, while the CdS cell prepared under the same conditions had efficiency of 9%. Fill factor and photocurrent values were comparable. Anyway this has opened up the scope for Cd free cells.

1.2.6 ZnS, Cd$_x$Zn$_{1-x}$S and ZnSe

These are few other materials that could be prepared by CBD technique, which finds applications in photovoltaic devices [24]. It is expected that in CdS based solar cells the use of wider band gap materials such as ZnS or Cd$_x$Zn$_{1-x}$S can lead to decrease in window absorption losses and improvement in the short circuit current of the cell.

Reports have shown that it is not easy to prepare high quality ZnS by CBD, though Paul O' Brien has suggested strategies for the same [24]. Nair and Nair [91] have given the recipe as, 5 ml of 1 M zinc sulfate, 4.4 ml of NH$_3$/NH$_4$Cl (pH 10), 54 ml of 50% TEA, 2 ml of 1 M thioacetamide and the rest deionised water to make up to 100 ml by volume. Deposition of ZnS films of 0.2 μm thickness could be obtained at 50°C by about 6 hrs or at room temperature by about 20 hrs.

Cd$_x$Zn$_{1-x}$S is a more promising material for photovoltaic cells due to the possibility of tailing its semiconductor properties between the values corresponding to the pure binaries. This fact allows to adjust the material properties as per the device requirements. The techniques adopted for preparation of Cd$_x$Zn$_{1-x}$S include evaporation, CVD, spray, electrodeposition, SILAR and CBD. Dona et al. [92] has prepared this phase by CBD using 1.4 M 5% ammonia, 2.25 M 80% hydrazine, 0.14 M thiourea and CdSO$_4$ and ZnSO$_4$ concentration between 0 and 0.1 M, i.e. [ZnSO$_4$] + [CdSO$_4$] = 0.1 M. CdSO$_4$ and ZnSO$_4$ were added first to the NH$_3$/NH$_2$-NH$_2$ solution under stirring followed by the addition of thiourea solution. The temperature of deposition was 70°C.
Fig.(1.9) (a) Output characteristics of thin film CuInS$_2$ solar cells with CdS and ZnO buffer layers
(b) Spectral quantum efficiencies of thin film CuInS$_2$ solar cells with CdS and ZnO buffer layers
P.K. Nair et al. [15] has found ZnSe to be more photosensitive than ZnS. The preparation suggested was, 35 ml of 0.1 M zinc acetate, 16 ml of 0.8 M sodium citrate, 5 ml of 7.4 M ammonium hydroxide mixed with 20 ml of 0.07 M N,N dimethyl selenourea and the volume made up to 100 ml with deionised water. Depositions could be made at room temperature or at 60°C.

1.2.7 Bi$_2$S$_3$ and Bi$_2$Se$_3$

Sulfides and selenides of bismuth are also finding their place in the field of photovoltaics. P. K. Nair et al. [45,93] prepared Bi$_2$S$_3$ from a bath of 10 ml of ~0.5 M Bi(NO$_3$)$_3$. 5 H$_2$O solution, 8 ml of 50% triethanol amine and 4 ml of 1 M thioacetamide made up to 100 ml. The duration of deposition was 24 hrs.

Similarly, the same group has reported the deposition of Bi$_2$Se$_3$ thin films from a bath consisting of 7 ml of 0.5 M Bi(NO$_3$)$_3$ solution, 7 ml of 50% triethanolamine an 20 ml of 0.07 M N,N-dimethyl selenourea solution finally made up to 100 ml. Films of 0.2 μm thickness could be deposited in about 9 hrs at 40°C or in about 60 hrs at room temperature [94].

1.2.8 Indium hydroxy sulfide

Most recent trend in R&D activities in solar cell include the idea of fabricating chalcopyrite based devices replacing the CdS buffer layer by other CBD compounds with similar or even better properties [95]. One promising candidate to achieve this goal is the CBD-prepared indium hydroxy sulfide. In(OH)$_x$S$_4$ when used as buffer layer in solar cells gave good I-V characteristics [96,97]. Some of the thin film properties of this material are mentioned in Ref. [98].

Conditions of chemical bath deposition that lead to good quality indium hydroxy sulfide thin films with high growth rate were [99]- [In Cl$_3$] = 0.025 M, [thioacetamide] = 0.1 M and [acetic acid] = 0.1 M at 70°C and at acidic pH. A terminal thickness of 1800Å was obtained after 45 min of deposition. XPS analysis showed the as-prepared samples to be consisting of more than 80% indium hydroxy sulfide and some quantities of indium oxide and indium sulfate. The molecular formula suggested for this phase was close to InOH$_x$S with slight variation in the OH:S proportion.
1.2.9 *Copper indium diselenide (CIS) (CuInSe₂)*

In the field of heterojunction solar cells, CuInSe₂ has a potential scope with its attractive properties of direct band gap (~1 eV), high optical absorption coefficient ($\alpha \sim 10^5 \text{ cm}^{-1}$), good lattice match and electron affinity with other binary semiconductors such as CdS. In recent times, CuInSe₂ thin film based single junction solar cells have shown efficiencies as high as 18.8% [100].

There are various preparation techniques reported for this material [101]. However all these techniques involve sophisticated and expensive set up. Moreover, handling of poisonous gases like H₂Se or selenium vapour is a major problem in many of these processes. It is in this context that the significance of chemical bath deposited CIS arise.

The first report on CBD-CIS came in the year 1987 [102]. The preparation procedure was as follows: 10 ml of 0.5 M copper chloride solution was mixed with 6 ml of 7.4 M triethanolamine and 20 ml of 13.4 M ammonia solution. To this mixture 18 ml of 0.5 M freshly prepared sodium selenosulfate solution was added to get a resulting pH of 10. The deposition mixture was magnetically stirred during the growth process and the duration of depositions was standardized at 30 min. It was observed that at low temperatures of deposition (~50°C), Cu reacts much faster with selenium than In does. This resulted in the incorporation of CuSe phase. The stoichiometry of the as-prepared films deposited at 50°C and 90°C were evaluated as Cu₁₀In₁Se₂₀₂ and Cu₀₀₁In₁Se₁₈₅ respectively, from EDS analysis.

In the next year (1988) there was a report on fabrication of a junction on a trial basis [103]. CuInSe₂ preparation was reported as: Cu²⁺ ions were complexed with ammonia solution and mixed with Na₂SeSO₃ solution. To this mixture, solution containing a complex ion of indium and citrate was added. The reaction was carried out at 40°C for 14 hrs to obtain uniform films of CuInSe₂ on glass and quartz substrates. The XRD analysis showed a chalcopyrite structure. While EPMA analysis revealed the composition to be nearly stoichiometric, Hall measurements showed that the films were p-type with a carrier concentration of about $10^6 \text{cm}^{-3}$, $\mu_h \sim 1 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and conductivity of about $10^3 \Omega^{-1}\text{cm}^{-1}$. The photosensitivity of the film was found to be maximum when annealed at temperature greater than 450°C.

A p-CuInSe₂/n-Si hetero junction was tried by depositing this CIS layer of 2 µm thickness on a Si wafer of 1 Ωcm resistivity. This cell suffered from large series
resistance that lead to deterioration of short circuit current and fill factor. After a heat treatment of the device at 520°C in air for 30 min, the open circuit voltage was 300 mV. However in general the junction performance was not appreciable.

In the year 2000, there was a report on CBD-CIS [101]. The deposition bath consisted of CuCl₂, InCl₃, H₂SeO₃ and LiCl dissolved in deionised water. The pH of the bath was adjusted to 2.2 by adding dil. HCl. EDAX analysis showed the composition of the surface layer of the film to be close to the required stoichiometry. However the composition determined by ICP analysis deviated much from the EDAX results. Hence it was inferred that an indium rich region is formed near the surface and a Cu rich region is formed towards the bottom. For the same reason, the as-prepared films could only be considered as a good precursor for CIS films. The film property was found to improve with annealing in Se atmosphere.

The first report on device level CuInSe₂ thin film by chemical deposition is from the Photovoltaic lab of Cochin University of Science and Technology [104]. The details are already included in section (1.2.1.h) under the heading ‘All-CBD cell’.

1.2.10 Copper indium disulfide (CuInS₂)

The ternary compound semiconductor of CuInS₂ is an attractive material for solar energy conversion as its band gap is 1.55 eV. A number of deposition techniques are used for the synthesis of this material. This includes single, dual and three source evaporation, spray pyrolysis, RF sputtering, electrodeposition and sulfurisation. The highest conversion efficiency attained with this material was 7.3% [105].

G.K. Padam et al. has reported the preparation of this material by CBD [106]. The deposition mixture consisted of 10 ml CuCl₂·2H₂O (0.5 M), 5.5 ml InCl₃ (0.5 M), 40 ml thiourea (0.5 M), 6 ml triethanolamine (0.5 M) and 20 ml ammonia (13.4 M). The deposition was carried out at 80°C and the duration of deposition was 45 min. Films obtained were found to be extremely adherent to the glass substrate and homogenous in appearance when stirring was given to the mixture, where as unstirred films gave powdery appearance. X-ray analysis proved this material to be crystalline but with slight deviation from the standard d-values of CuInS₂. Both the EDS and the spectrochemical methods showed that the Cu to In ratio is 1.08 instead of 1.
1.2.11 Copper selenide

Cu$_2$Se is a cuprous chalcogenide film that always show p-type conduction due to copper vacancies. This material has an indirect band gap 1.1-1.27 eV [107], which makes it an absorber material and a direct band gap > 2eV [108], which makes it a window material in solar cells. Photovoltaic junctions Cu$_2$Se/Si, Cu$_{2-x}$Se/CdS, Cu$_{2-x}$Se/CdSe and Cu$_2$Se/InP are reported. Prospects for this material also lies in the feasibility of producing the ternary compound CuInSe$_2$, starting with Cu$_{2-x}$Se precursor. Though there are various deposition techniques for this material, CBD is the simplest. Chapter 2 elaborates the preparation technique and applications of this material in photovoltaics.

1.3 Conclusion

The principle behind chemical bath deposition technique is the controlled precipitation of a compound from a reaction bath. Nature of reactants and substrates and the temperature and pH of the reaction are few of the factors that influence the deposition process.

Semiconducting thin films prepared using CBD find applications as photo detectors, solar control coatings and solar cells. In the field of solar cells, apart from the direct use of CBD films of binary compounds, there is also scope for use of films like Cu$_x$S and Cu$_2$Se as a precursor for preparing the leading materials such as CuInS$_2$ and CuInSe$_2$. Efforts in this direction by diffusing indium into these binary CBD films have been reported from Photovoltaic laboratory, Dept. of Physics, Cochin University of Science and Technology [109].

Theoretical modeling of thin film deposition by this technique has been an area of constant interest among researchers [110]. The advantages of CBD include simplicity and low cost of the procedure, minimum wastage of chemicals and possibility of deposition on large areas. In this chapter the disadvantages of this technique are also described in detail. Few CBD based cells are highlighted along with the reported cell efficiencies. The preparation procedures of various thin films by this chemical method, that finds application in photovoltaics are also briefly mentioned.
The Photovoltaic division of Cochin University of Science & Technology has been working in this field of CBD thin films for the past few years. PbS, CdS, Cu_xS, CuInSe_2 etc. has been our material of constant interest. An ‘All-CBD cell’ with CdS/CuInSe_2 junction was fabricated in this lab [66]. Though the efficiency was only around 3%, it has opened the avenue for large area-low cost thin film solar cells. Recently our interest has been slowly shifting towards relatively new materials that may turn out as successful candidates of tomorrow. This thesis work forms a part of our sincere endeavor in this direction.
Reference


