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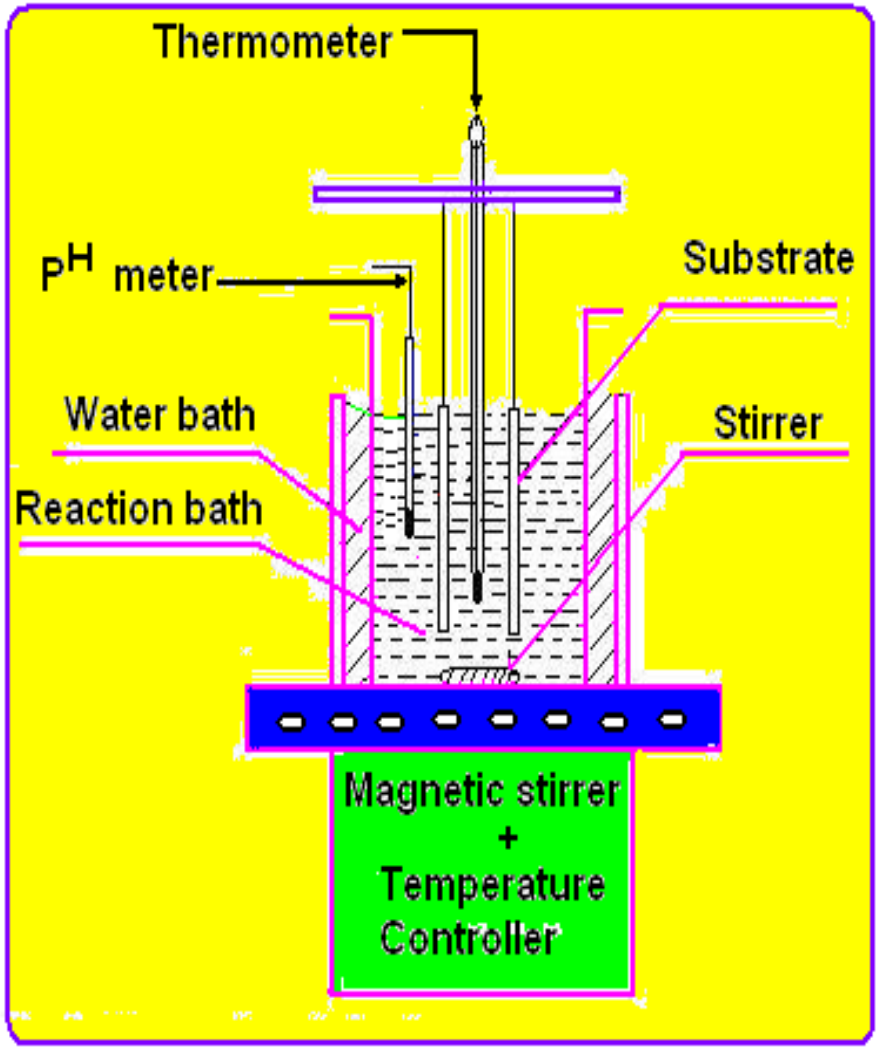
Date :

CBD



Preparative parameters on film thickness
No. of deposition, pH, Anion conc, Doping, Temperature, bath composition, Substrate rotation

- **Growth of thin films in the bulk precipitation of the solution**
- **Growth of thin films at the surface of the solution due to the precipitation**

- Inexpensive, simple and convenient for large area deposition
- Low temperature process so variety of substrates such as metal, semiconductor, insulator and polymer can be used. It avoids corrosion or oxidation of metallic substrates
- Slow process which facilities better orientation of crystalline with improved grain structure
- It results in to pinhole free and uniform deposits as the solution always remains in touch with the substrates
- Stoichiometric deposits are obtained science the basic building blocks are ions instead of atoms
- The preparative parameters are easily controllable

Chemical bath deposition

The technique of CBD involves the controlled precipitation from solution of a compound on a suitable substrate.. Factors such as control of film thickness and deposition rate by varying the solution pH, temperature and reagent concentration are allied with the ability of CBD to coat large areas, in a reproducible and low cost process. In addition, the homogeneity and stoichiometry of the product are maintained partly by the solubility product (Ksp) of the material in question. The first report of CBD was in 1884 by J. E. Reynolds (*J. Chem. Soc.*, **45**, 1884, 162) for the deposition of PbS.

Drawbacks

Major drawback of the CBD process is the inefficiency of the process, in terms of the utilization of starting materials and their conversion to thin films. The extent of the heterogeneous reaction on the substrate surface is limited by two major factors, the competing homogeneous reaction in solution (which results in massive precipitation in solution) and deposition of material on the CBD reactor walls.

Concept of Solubility and Ionic Product of CBD

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 equilibrium is established between the solid phase and ions in the solution as

$$AB\ (S) = A^+ + B^- \qquad (1)$$

Applying law of mass action to this equilibrium,

$$K = C_A{}^+ C_B{}^- / C_{AB}\ (S) \qquad (2)$$

Where, $C_A{}^+$, $C_B{}^-$ and C_{AB} are concentrations of A^+, B^- and AB in the solution respectively.

The concentration of a pure solid phase is a constant number i. e.

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

$$K = C_A{}^+ + C_B{}^- / K'$$

$$\text{Or} \quad K\,K' = C_A{}^+ + C_B{}^- \qquad (4)$$

Since K and K' are constant, the product K K' is also constant, say Ks, therefore equation (4) becomes,

$$K_S = C_A{}^+ + C_B{}^- \qquad (5)$$

Ks is called solubility product (SP) and $(C_A{}^+ + C_B{}^-)$ is called as the ionic product (IP). When the solution is saturated, the ionic product is equal to the solubility product. But when IP exceeds the SP i.e. IP/SP = S > 1, the solution is supersaturated, precipitation occurs and ions combine on the substrate and in the solution to form nuclei. Solubility product is affected by temperature, solvent and particle size.

CdSe (CBD)

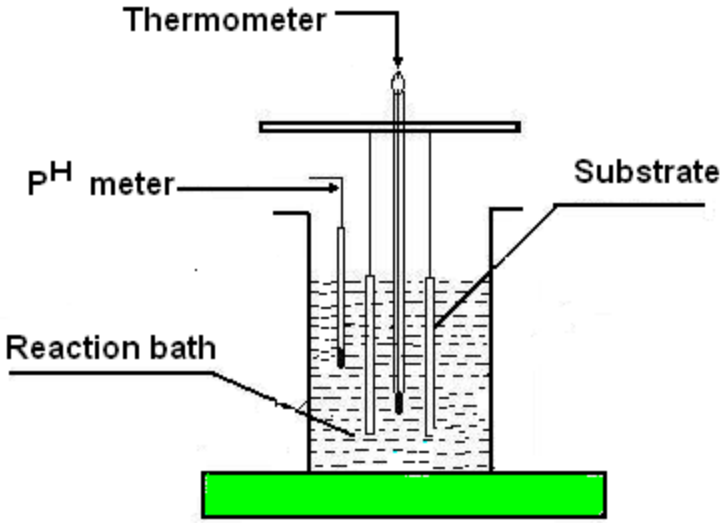


Fig. Experimental set up to deposit CdSe film

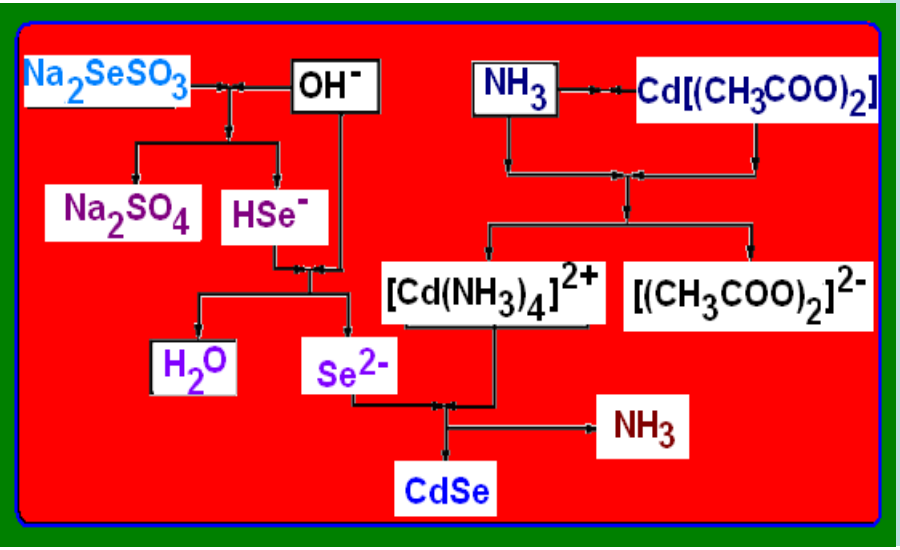


Fig. Reaction mechanism for CdSe thin films

Reaction mechanism:

The CdSe deposition was carried out according to the following steps:

Sodium selenosulphate (Na_2SeSO_3) hydrolyses in the solution to give Se^{2-} ions according to

$$Na_2SeSO_3 + OH^- \rightleftharpoons Na_2SO_4 + HSe^- \quad (1)$$

$$HSe^- + OH^- \rightleftharpoons H_2O + Se^{2-} \quad (2)$$

When ammonia solution is added in Cd-salt solution to form the complex cadmium tetra-amine ion $[Cd(NH_3)_4^{2+}]$ as,

$$Cd^{2+} + 4NH_3 \rightleftharpoons Cd(NH_3)_4^{2+} \quad (3)$$

Then $Cd(NH_3)_4^{2+}$ react with Se^{2-} ions and formation CdSe thin film as follows:

$$Cd(NH3)_4^{2+} + Se^{2-} \rightarrow CdSe + 4NH_3 \quad (4)$$

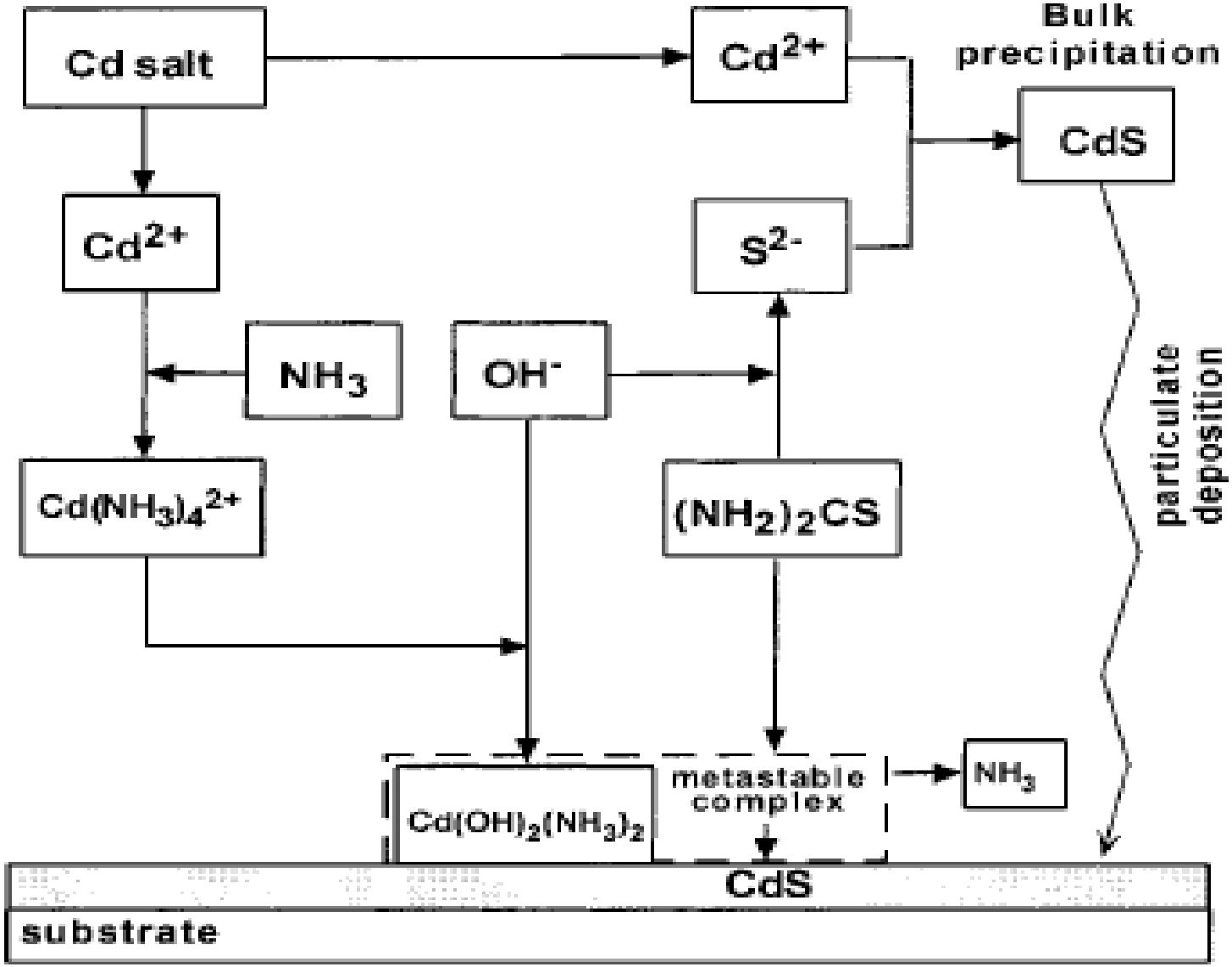


Figure 1. Schematic of the CBD process. CdS film may grow by decomposition of a metastable complex [$Cd(OH)_2(NH_3)_2SC(NH_2)_2$] on the surface (preferred mechanism) and by nuclei/particle deposition from the bulk.

Deposition of thin films by chemical methods

- Growth of thin films in the bulk precipitation of the solution
- Growth of thin films at the surface of the solution due to the precipitation

Preparative parameters on film thickness

- ❖ pH
- ❖ Temperature
- ❖ Anion concentration
- ❖ Substrate
- ❖ Composition
- ❖ Doping
- ❖ Substrate rotation
- ❖ No. of deposition

CHEMICAL BATH DEPOSITION (CBD)

- *Oxides:* ZnO, Bi_2O_3, CdO, CuO, MnO, TiO_2
- *Sulphides:* CdS, CdZnS, ZnS, Bi_2S_3, Sb_2S_3, As_2S_3, PbS, HgS, HgCdS, MnS, CuxS, Ag_2S, SnS, SnS_2, In_2S_3, FeS_2,$CdCr_2S_4$, $HgCr_2S_4$
- *Selenides:* CdSSe, ZnSe, CdSe, HgSe, PbSe, Bi_2Se_3, Sb_2Se_3
- Metals: Ag, Cu

Reaction mechanism for CdS preparation

- Cadmium sulphate react with ammonia to form complex compound
- $CdSO_4 + 4NH_3 \longrightarrow [Cd(NH_3)_4]SO_4$
- Dissociation of thiourea I alkaline medium
- $NH_2 \quad NH_2$
- $C + CH^- \longrightarrow CH_2N_2 + H_2O + HS^-$
- S
- Formation of divalent sulphide ions
- $HS_2 + OH^- \longrightarrow S^{--} + H_2O$
- Formation of cds
- $Cd(NH_3)^{2+} + S^{--} \longrightarrow CdS + 4NH_3$