

PREPARATION OF THIN FILM ELECTRODES FOR ELECTROCHEMICAL SOLAR CELLS — CHEMICAL BATH DEPOSITION

C V SURYANARAYANA,

Emeritus Scientist, Anna University, Madras-600 032,

A S LAKSHMANAN, V SUBRAMANIAN and R KRISHNAKUMAR

Central Electrochemical Research Institute, Karaikudi-623 006

ABSTRACT

Many methods are available for the preparation of thin films of semiconductors used as photoelectrodes in photoelectrochemical cells. In this article, Chemical Bath Deposition (CBD) is discussed. The emphasis is on thin films particularly for use in solar energy conversion application through the electrochemical route.

Key Words: Electrochemical solar cells, thin film electrodes, chemical bath deposition.

INTRODUCTION

Preparation of thin film photoactive materials plays an important part in devising photoelectrochemical solar cells. Thin film photoactive electrodes have the overriding advantages of ease of preparation and cheapness due to the very small quantity of the active material required.

Some of the more common thin film preparation methods are chemical spray deposition (CSD), chemical bath deposition (CBD), electrodeposition, vacuum co-evaporation, chemical vapour deposition (CVD) and RF sputtering. The processes produce polycrystalline thin films satisfactory for end use in photoelectrochemical (PEC) cells. This article presents briefly chemical bath deposition (also known as solution growth method, controlled precipitation method, electrodeless plating or simply chemical deposition) for producing thin semiconductor films.

Advantages of CBD

CBD does not require sophisticated instrumentation like vacuum systems and other expensive equipment. It can be carried out in a glass beaker. Only a hot plate and a stirrer are the equipment needed and hence the power consumption is also negligible. The starting chemicals are commonly available and cheap materials.

CBD is ideally suited for large area deposition; it can be done by using large volume vessels. A large number of substrates can be coated in a single run with a proper jig design. Positioning the substrates along the wall of the reaction vessel is a simple procedure to have a large number coated. Unlike in electrodeposition, electrical conductivity of the substrate is not a necessary requirement for CBD. Hence, any insoluble surface to which the solution has free access will be a suitable substrate for deposition. The low-temperature deposition used in CBD avoids oxidation or corrosion of metallic substrates. CBD results in pin hole free and uniform deposits as the solution from which the films are deposited always remains in touch with the substrate. Finally, stoichiometric deposits are easily obtained, since the basic building blocks are ions (instead of atoms) in CBD.

In CBD, the film forms slowly, which facilitates better orientation of crystallites with improved grain structures. Depending upon the deposition conditions such as the bath temperature, stirring rate, pH, solution concentration and its purity and quality of the substrate, the film growth can take place by ion-by-ion condensation of the material on the substrate or by adsorption of the colloidal particles from the solution of the substrate. The process of precipitation of a substance from the solution onto a substrate depends mainly on the formation of a nucleus and subsequent growth of the film.

The concept of nucleation in solution is that the clusters of molecules formed undergo rapid decomposition and particles combine to grow up to a certain thickness of the film beyond which no further building up of thickness occurs.

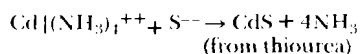
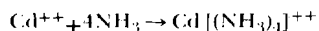
Preparation of polycrystalline films

Using CBD, polycrystalline films of CdS [1-5], CdSe [6-11], CdTe [12], CuInSe₂ [13], Bi₂S₃ [14], Bi₂Se₃ [15], PbS [16-21], PbSe [6, 22], Ag₂S [23], TiSe [24] and ZnSe [25] have been prepared. Thiourea or thioacetamide as a sulphur source, selenourea or sodium selenosulphate as a selenium source and TeO₂ as a tellurium source have been employed to prepare the chalcogenides in alkaline medium along with the desired cation.

Cadmium sulphide thin film

CdS thin films are generally prepared by controlled precipitation from a solution containing a cadmium complex and an organic sulphur-bearing compound such as thiourea which is added at a slow rate to have a controlled and slow precipitation of CdS. Thin films (0.8-2 μ thick) have been obtained [2, 4] by the controlled reaction between cadmium tetraammonium sulphate, cadmium sulphate or cadmium acetate and thiourea in solution in a temperature range of 75-90°C and pH of 9-10 on substrates of nickel, aluminium and copper. The deposition duration was around 30 minutes with the substrates being rotated at a constant speed of 70-100 rpm to ensure continuous exposure of the depositing surface to the fresh medium so as to result in the formation of uniform deposits.

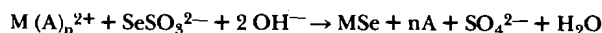
The chemical reactions involved can be broadly given as follows:



The films prepared by this process are claimed to be not affected by oxygen and moisture ambients. In, Ag, As and Cu in the form of their halides have been used for doping the CdS films. An interesting observation was that films without incorporating dopants were polycrystalline and with dopants amorphous. The CdS films were polycrystalline in nature with mixed FCC (NaCl) and wurtzite structure. A solvent medium of triethanolamine has also been reported [5].

Cadmium selenide thin films

The preparation of CdSe by CBD [6, 8-11] by solution growth method on a variety of substrates (metal foils, metal films, insulators and semiconductors) has been studied under different deposition parameters such as pH, rate of stirring etc. Sodium selenosulphate has been suggested [7] instead of selenourea which is unstable. The mechanism for CdSe and PbSe deposition involves the following general reaction step [6].



where M is Cd or Pb and A is a complexing agent (NH_3 , OH^- or citrate) for the metal salt such as acetate or sulphate.

The film formation depends upon an initial nucleation step. The $Cd(OH)_2$ present in the solution and also that formed on the substrate form the nucleus for the subsequent deposition of CdSe film, whose rate of deposition increases with increase in pH. At room temperature ($\sim 28^\circ C$) with excess of NH_4OH no film or precipitate forms quickly due to the solubility of Cd^{2+} and Se^{2-} . At higher temperatures, the concentrations of Cd^{2+} and Se^{2-} increase due to the dissociation of the Cd complex and selenourea or sodium selenosulphate and the deposition begins. Mixed hexagonal and cubic phases were observed in CdSe films deposited from a bath having a suspension of $Cd(OH)_2$ while cubic phases were observed with clear solutions [6].

To have uniform and quality deposits, it has been recommended that the substrates be soaked in a suspension of $Cd(OH)_2$ at $50^\circ C$ for 5 minutes before deposition. This helps in the formation of nucleation sites. The deposition is carried out at $80-90^\circ C$ with occasional stirring for 30 to 60 minutes [10, 11] to get a transparent red film of CdSe. After the initial deposition, the plates are heat-treated around $500^\circ C$ for 15 minutes to improve adhesion. After the heat-treatment the substrates are soaked again in $Cd(OH)_2$ suspension and subsequent plating is carried out. No further heat treatments are necessary for subsequent depositions. After the final deposition, the films are activated by heat sensitizing in air around $550^\circ C$ for 30 minutes to obtain good photovoltaic properties.

Cadmium telluride thin film

Thin films of CdTe have been deposited by CBD on conducting glass substrates and Ti plates [12] around $40-60^\circ C$ using equimolar concentrations of $Cd(Ac)_2$ and TeO_2 . TeO_2 is added to NaOH and the pH is adjusted to ~ 2 by addition of H_2SO_4 . It has been observed by annealing at $590^\circ C$ for 30 minutes that the Cd:Te ratio changes from $\sim 25:60$ to $\sim 55:45$.

Copper-indium selenide thin film

Thin films of $CuInSe_2$ have been prepared [13] by the solution growth method involving a slow reaction of the complex formed by triethanolamine with both In^{3+} and Cu^{2+} and sodium selenosulphate at room temperature to get a thickness of 200-300 Å. Annealing in argon gas results in crystalline films.

Bismuth sulphide and bismuth selenide thin films

Bi_2S_3 films have been prepared [14] by the slow reaction method. At a pH of 8, the triethanolamine complex of Bi^{3+} is allowed to react with S^{2-} ions, which are released slowly by the dissociation of thiourea. A thin film of Bi_2S_3 of thickness of 0.5 to 1 μ is obtained at a bath temperature of $100-110^\circ C$ (for 40 minutes) and allowing the reaction to continue at room temperature for 4 to 5 hours. The films are of n-type with a resistivity in the range of $(10-30) \times 10^6 \Omega cm$. The mechanism of deposition of Bi_2S_3 is similar to that of Pb-chalcogenides [16-18].

Unlike Bi_2S_3 , Bi_2Se_3 can be deposited [15] at room temperature by the reaction between ammoniacal triethanolamine complex of Bi^{3+} and sodium selenosulphate. The deposition goes to completion in about 2

hours. By the addition of hydrazine hydrate, thin films of Bi_2Se_3 with a metallic lustre, good electrical conductivity and thickness in the range of 0.1-0.2 μ can be formed in a shorter time of about 30 minutes.

Acknowledgement

The authors wish to thank Dr V K Venkatesan, Head, Division of Electrochemical Material Science for his kind encouragement.

REFERENCES

1. N R Pavaskar, C A Menezes and A P B Sinha, *J Electrochem Soc*, **124** (1977) 743
2. S Chandra, R K Pandey and R C Agrawal, *J Phys D*, **13** (1980) 1757
3. Inderjeet Kaur, D K Pandya and K L Chopra, *J Electrochem Soc*, **127** (1980) 943
4. S H Pawar and L P Deshmukh, *Mater Chem Phys*, **10** (1984) 83
5. R C Bhardwaj, C M Jadhav and M M Taqui Khan, *Solar Cells*, **12** (1984) 371
6. R C Kainthla, D K Pandya and K L Chopra, *J Electrochem Soc*, **127** (1980) 277
7. G A Kitaev and T S Terekhova, *Russ J Inorg Chem*, **15** (1970) 25
8. K Rajeswar, L Thompson, P Singh, R C Kainthla and K L Chopra, *J Electrochem Soc*, **128** (1981) 1744
9. D R Pretz, M E Langmuir, R A Boudreau and R D Rauh, *J Electrochem Soc*, **128** (1981) 1627
10. R A Boudreau and R D Rauh, *J Electrochem Soc*, **130** (1983) 513
11. R C Kainthla, J F McCann and D Haneman, *Solar Energy Mater*, **7** (1983) 491
12. R N Battacharya, K Rajeswar and R N Noufi, *J Electrochem Soc*, **131** (1984) 939
13. R N Battacharya, *J Electrochem Soc*, **130** (1983) 2040
14. P Pramanik and R N Bhattacharya, *J Electrochem Soc*, **127** (1980) 2087
15. P Pramanik, R N Bhattacharya and A Mandal, *J Electrochem Soc*, **127** (1980) 1857
16. J Bloem, *Appl Sci Res*, **6B** (1956) 92
17. F Kicinski, *Chem and Ind*, **67** (1948) 54
18. H N Acharya and H N Bose, *Phys Status Solidi (a)*, **6** (1971) K43
19. H N Venkoba Rao, J Kuppusami, R Lakshminarayanan, V Subramanian and C V Suryanarayana, *Ind J Technol*, **3**, (1965) 60
20. K K Janardhanan Pillai, Y V P Ramachandra Row, H N V Rao, K Ramakrishnan, V Subramanian, K Sundararajan and C V Suryanarayana, *Ind J Pure Appl Phys*, **8** (1970) 831
21. V Subramanian, H N Venkoba Rao, K K Laroia and C V Suryanarayana, *Ind J Technol*, **3** (1965) 248
22. R A Zingaro and D O Skovlin, *J Electrochem Soc*, **111** (1964) 42
23. Miss Mary Juliana Mangalam, K Nagaraja Rao, N Rangarajan and C V Suryanarayana, *Ind J Pure Appl Phys*, **7** (1969) 628
24. Mary Juliana Mangalam, K Nagaraja Rao, N Rangarajan, M I A Siddiqi and C V Suryanarayana, *Jap J Appl Phys*, **8** (1969) 1258
25. G A Kitaev and T P Sokolova, *Russ J Inorg Chem*, **15** (1970) 176