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SOLUTION SYNTHESIS OF

CHALCOGENIDES

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Summary

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Abstract

Polycrystalline chalcogenide thin films are of interest in photovoltaic cells. These wide area electronic devices need low cost fabrication methods. Solution methods offer this advantage and are also capable of producing films and scaling to an industrial level.

This report gives a brief literature survey of the Chemical Bath Deposition method for CdS and CoS. The speciation of the Cd in alkaline solution is calculated using the Octave programming environment.

A literature survey of electrodeposition of chalcogenides as an alternative to the coprecipitation of the Chemical Bath deposition method is described.

Introduction

A primary requirement of photovoltaics for mass application is low cost, which can be reduced by adopting thin film materials, deposited on inexpensive substrates. Naturally, this must be accompanied by low manufacturing costs, in terms of equipment, wide area deposition and rapid production. Vacuum or closed chamber techniques, needed to fabricate viable semiconductor p-n junctions, currently, are not very economical. Some photovoltaic cells such as CdTe-CdS or $CuInSe_2$-ZnO can be very efficient even as polycrystalline material and as thin films on inexpensive substrates. These also lend themselves to chemical solution deposition methods.

Chemical deposition methods use chemical reactions of precursors to grow films from a dispersed phase, be it either gaseous or liquid. Those include metal organic vapour phase deposition (MOCVD) and from the liquid phase there are chemical bath, electrodeposition and sol gel. Generally, they, have several notable advantages; reactants can be transported over the whole surface to be covered resulting in homogeneous coatings over large areas; the chemistry can be adapted to reduce deposition temperatures and rates; some methodologies, particularly solution methods do not envisage closed chambers.

Chemical bath deposition (CBD) does not require expensive equipment as glass reaction vessels and substrate holders may be used, moreover, they can be scaled up to coat large areas. Many sulphides have low solubility products in water, a property that is used to perform qualitative analysis of dissolved metals. Controlled precipitation from dissolved salts could then be used to prepare fine sulphide powders or thin films, from soluble metal salts. Reynolds [1] deposited PbS thin films by CBD using thiourea as the sulphurous reagent.

Normally, the pH and temperature need to be regulated to achieve controllable growth conditions. Figure 1 illustrates schematically a typical lab bench experiment.
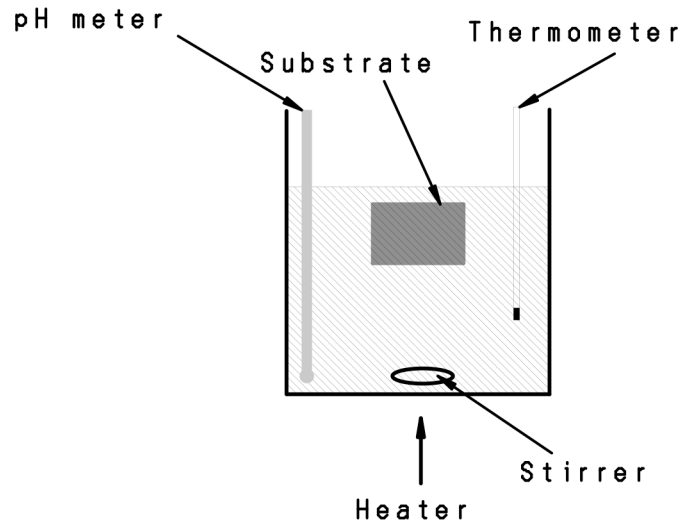
**Fig. 1 Basic chemical bath deposition apparatus.**

Han et al [2] grew thin films on 2x2 cm^2 soda lime glasses coated with fluorine doped SnO$_2$. CdS films were prepared from aqueous solution, which contained 1.5x10^{-3} mol/L of cadmium acetate and 5x10^{-2} mol/L of thiourea. Ammonia was used to adjust the solution pH to 11 at room temperature. The bath temperature was kept constant at 75 °C for a deposition time of 60 min. The thickness of the standard CBD CdS film was about 150 nm. Sample B was prepared by the standard process, followed by annealing in UHV using CdCl$_2$ vapour at 300 °C for half an hour. The thickness of sample B was around 150 nm, which was almost the same as that of the standard CBD CdS film. Sample C was made first by the standard CBD CdS process with reduced deposition time (20 min) and then an additional low temperature chemical bath of CdS layer. The solution temperature of the second treatment was kept at 55 °C for 20 min. The final sample C had the same CdCl$_2$ annealing treatment as sample B. The total thickness of the bi-layer CdS film was about 80 nm. All the CdS films were finished into solar cells. When all CdS films finished CdTe/CdS solar cell devices were fabricated. A 5 mm CdTe layer was deposited by close space sublimation at source and substrate temperatures of 600 and 520 °C, respectively followed by a treatment ex-situ in CdCl$_2$, NP etching and gold back contact deposition. Finally the 2x2 cm^2 coated glass sheets were scribed using stainless steel needles into cells 5 x 5 mm^2.

At the EDL (University of Texas El Paso) [3] researchers prepared CdS by pouring sequentially cadmium acetate, ammonium acetate, ammonium hydroxide, and thiourea, all dissolved in deionised water, into a beaker and heating to temperatures between 85 to 90 °C. The reaction results in the deposition of CdS onto all surfaces in the bath, including the surfaces of the ITO coated glass. Typically, a 20-minute run yielded a film having a thickness between 800 and 1000.

Complexing agents can be used to control the reaction. Kumar et al [4] used triethylamine (TEA) to complex the cadmium as $[Cd(TEA)^{+2}]$. Solutions of 1 mol cadmium acetate dehydrate $Cd(OAc)_2.2H_2O$ and 0.125 mol thiourea were prepared in twice distilled water. Various volumes (4.2, 5.0, 5.6, 6.0, 7.0, 8.5, and 10.0 ml) of 25% NH_4OH and various molarities of TEA (0.2 0.4, and 1.0 mol) were used for studying their effects on the photoconductive properties of the films. The CdS deposition was carried out on commercial glass slides at a bath temperature of 80 °C for 2 hours. To form [Cd (TEA)] and $[Cd(NH_3)_n]$ complexes we stirred 5 ml of 1 mol $Cd(OAc)_2.2H_2O$ well with the desired volumes of 1 mol TEA 25% NH_4OH and 10 ml water in a 50 ml beaker. This solution was placed in a water bath, which was maintained at 85 – 90 °C and was allowed to reach the temperature of the solution flask at 80 °C. Finally, 5 ml of 0.125 mol thiourea was added and the temperature was maintained at 80 ° C for 2 hours.

Feitosa et al [5] deposited CdS thin films on glass ultrasonically degreased and cleaned commercial slide. The films were grown at 80 ℃ for ca. 55 minutes under continuous stirring. Three different aqueous alkaline solutions were made up with distilled and deionised water, and analytical-grade reagents. The EDTA concentration was changed from 0.6×10^{-4} M to 3.0×10^{-4} M, with steps of 0.3×10^{-4} M. In the group one, the solution containing cadmium sulphate $(CdSO_4)$ 0.003 M, thiourea 0.06 M, ammonia 2.3 M, and EDTA with four different concentrations, C1, C3, C5, and C7. In the group two the solution differs from the one by the addition of ammonia chloride (NH_4Cl), that forms a buffer-solution with ammonia to keep the pH = 11, and EDTA with four different concentrations, C2, C4, C6, C8. In the group three, the solution differs from the solution two by the addition of TX100 to the solution buffer.

Cadmium sulphide deposition takes place via the general reaction [6]:

$[Cd(NH_3)_n]^{2+} + SC(NH_2)_2 + x\, OH^- \rightarrow CdS + nNH_3 +$ other reaction products.
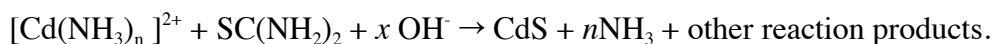
The decomposition products are a direct result of the hydrolysis reaction of thiourea in basic solutions. Fig. 3 shows the results of the analysis performed on the permeate after each run. It does not reveal the presence of cyanamide in the permeate as expected but that of guanidine and urea. Obviously, the cyanamide continues to react on the one hand with water to form urea and on the other hand with ammonia to form guanidine (reactions 2 and 3, Fig. 2). The total concentrations of urea and guanidine are not sufficient to explain the reaction mass balance. Hence, we must assume that further reactions of urea or guanidine take place in the permeate. The most probable reaction is the well-known urea decomposition to CO_2 (more likely CO_3^{2-} at this pH) and NH_3 (reaction 4, Fig. 2). This can explain the presence of CO_3^{2-} impurities found in the CdS film 4 . Furthermore, atomic absorption spectroscopy (AAS) measurements indicate an increased residual cadmium

concentration in the permeate after each CBD cycle (1st CBD cycle: 0.1 mg l, 8th CBD cycle: 0.9 mg l). An explanation could be the formation of cadmium complexes, but we are not able to make a statement about the kind of ligands involved.

Rakhshani and Al-Azab [7] grew on soda-lime glass substrates, in the range 70–90 °C. The alkaline solution (pH ≈ 11) consisted of $CdCl_2$ (2 mM), thiourea (3 mM), NH_4OH (640 mM) and NH_4Cl (≈15 mM). The glass substrates were etched in 2% HF (5 min) before deposition. The overall rate of deposition for films with a thickness 80–180 nm could vary from about 0.9 nm/min at 70 °C to about 8 nm/min at 90 °C. For the preparation of films thicker than ≈200 nm several runs of depositions, each from a fresh solution, were required.

Boyle et al used thioacetamide as an alternative to thiourea [8]. The CdS thin films were grown on commercial tin oxide (TO) glass substrates from solutions containing cadmium chloride (0.02 mo/l), urea (0.5 mol/l) and thioacetamide (0.2– 0.02 mol/l) to obtain a solution (100 cm^3) of final pH 5.5 – 4.9 (adjusted by addition of 5 M HCl or NaOH). The reaction mixture was maintained at the appropriate temperature (343 - 353 K) for deposition, with occasional stirring. Substrates were removed from the bath after the desired period of time, washed with de-ionised water and any adherent particulate matter removed by ultrasonic agitation. The substrates were allowed to dry under ambient conditions (ca. 2 h) before a further annealing step in air.

Cobalt Sulphides

The growth of cobalt sulphide films by CBD has been reported by Eze et al [9], the incorporation of $Co(OH)_2$ into the thin film was eliminated by optimizing both the chemical bath and the deposition time, The chemical bath was made up of 10 cc of 0.4 M cobalt chloride ($CoCl_2$) solution and 20 cc of ammonium hydroxide. 5 ml of 4 M sodium hydroxide solution and 10 ml of 1 M thiourea were then added, stirring continuously. The pH of the initial bath solution was between 10 and 11. Several bath constitutions were employed, varying the molar ratio of Co^{2+} to thiourea , NaOH and NH_3 (aq). The chemical reaction began with a greyish coloured solution slowly changing to deep brownish-purple. At the end of the reaction a clear brassy purple solution with dark precipitates was obtained. Film thicknesses ranged from 200 to 500 nm.

Speciation in cadmium solutions

Rieke and Bentjen [10] studied the deposition of CdS on silicon substrates and performed an extensive analysis of the solution equilibria. Speciation can be calculated knowing the relevant equilibrium constants this was performed using the Octave numerical package.

Cadmium hydroxide equilibrium

The data in Table 1 can be used to calculate the concentration and solubility of CdS at various values of pH as shown in Figure 1.

Table 1 Data used to calculate speciation of cadmium hydroxides in solution [10].

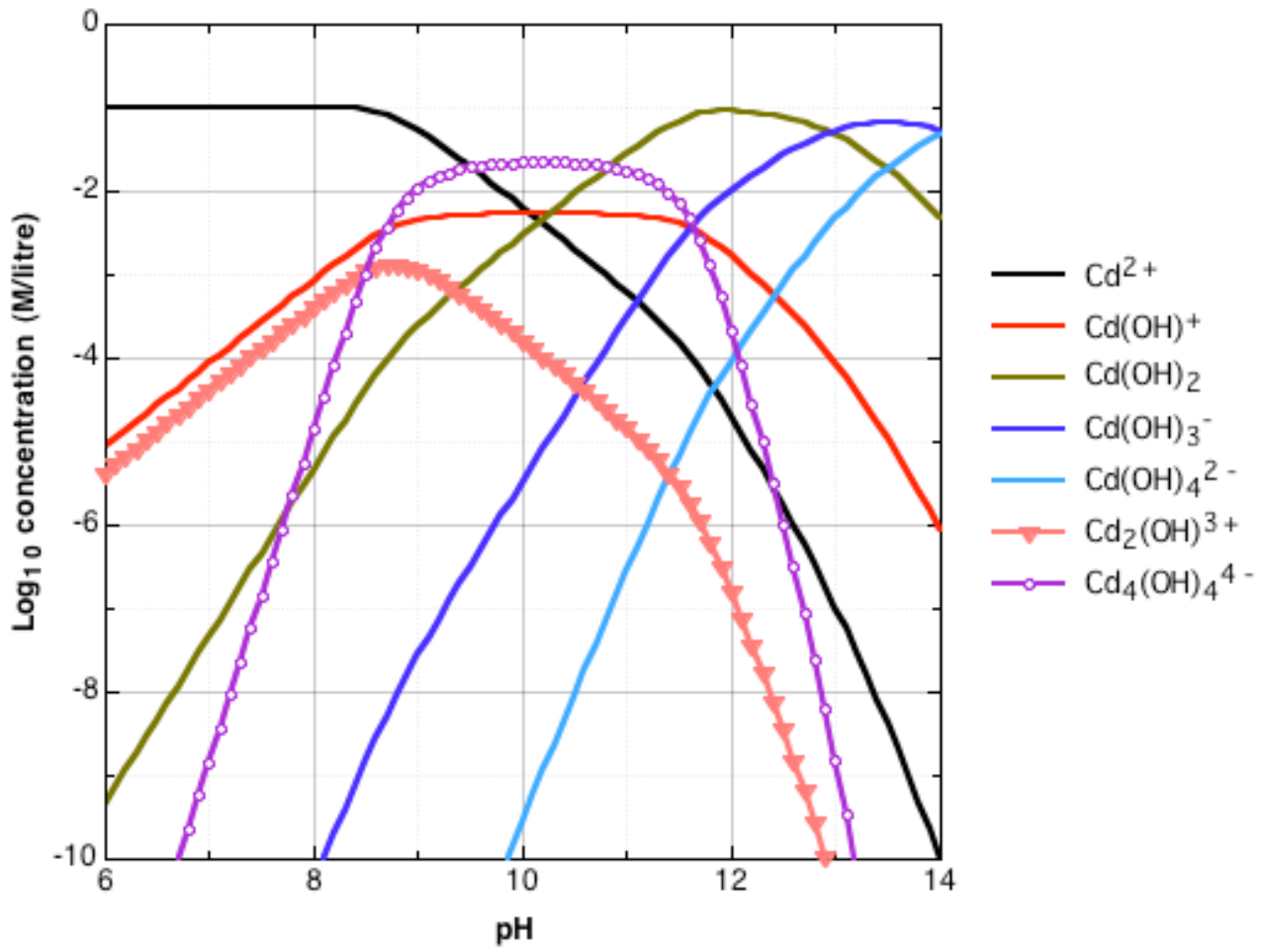| Reaction	Equilibrium constant
$Cd^{2+} + OH^- \leftrightarrow Cd(OH)^+$	$\log K11 = 3.92$
$Cd^{2+} + 2OH^- \leftrightarrow Cd(OH)_2$	$\log K12 = 7.65$
$Cd^{2+} + 3OH^- \leftrightarrow Cd(OH)_3^-$	$\log K13 = 8.70$
$Cd^{2+} + 4OH^- \leftrightarrow Cd(OH)_4^{2-}$	$\log K14 = 8.65$
$2Cd^{2+} + OH^- \leftrightarrow Cd_2(OH)^{3+}$	$\log K21 = 4.61$
$4Cd^{2+} + 4OH^- \leftrightarrow Cd_4(OH)_4^{4-*}$	$\log K44 = 23.15$

Figure 1 Speciation of cadmium hydroxides: log concentration versus pH.

Cadmium ion ammonia equilibrium.

Ammonia is added to solutions to adjust the pH and to complex the Cd^{2+} thus controlling the precipitation of CdS. The speciation of the Cd ammonium complexes are shown in Figure 2, calculated using the data in Table 2.

Table 2 Data used to calculate cadmium ammonia complexes in solution [10].

Reaction	Equilibrium constant
$NH_4^+ \leftrightarrow NH_3 + H^+$	pKa = 9.24
$Cd^{2+} + NH_3 \leftrightarrow Cd(NH_3)^{2+}$	logKN1 = 2.65
$Cd^{2+} + 2NH_3 \leftrightarrow Cd(NH_3)_2^{2+}$	logKN2 = 4.75
$Cd^{2+} + 3NH_3 \leftrightarrow Cd(NH_3)_3^{2+}$	logKN3 = 6.19
$Cd^{2+} + 4NH_3 \leftrightarrow Cd(NH_3)_4^{2+}$	logKN4 = 7.12
$Cd^{2+} + 5NH_3 \leftrightarrow Cd(NH_3)_5^{2+}$	logKN5 = 6.80
$Cd^{2+} + 6NH_3 \leftrightarrow Cd(NH_3)_6^{2+}$	logKN6 = 5.14
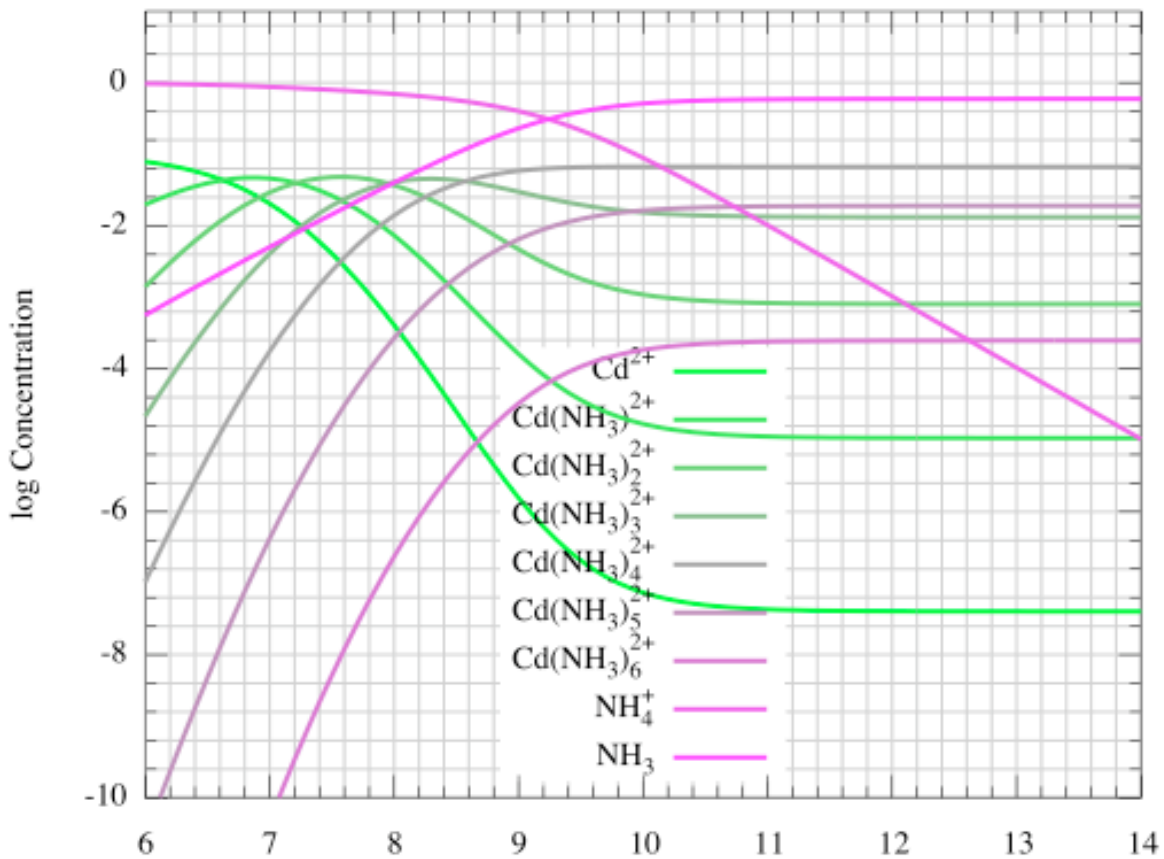
Figure 2 Speciation of Cd ammonium complexes: log concentration versus pH.
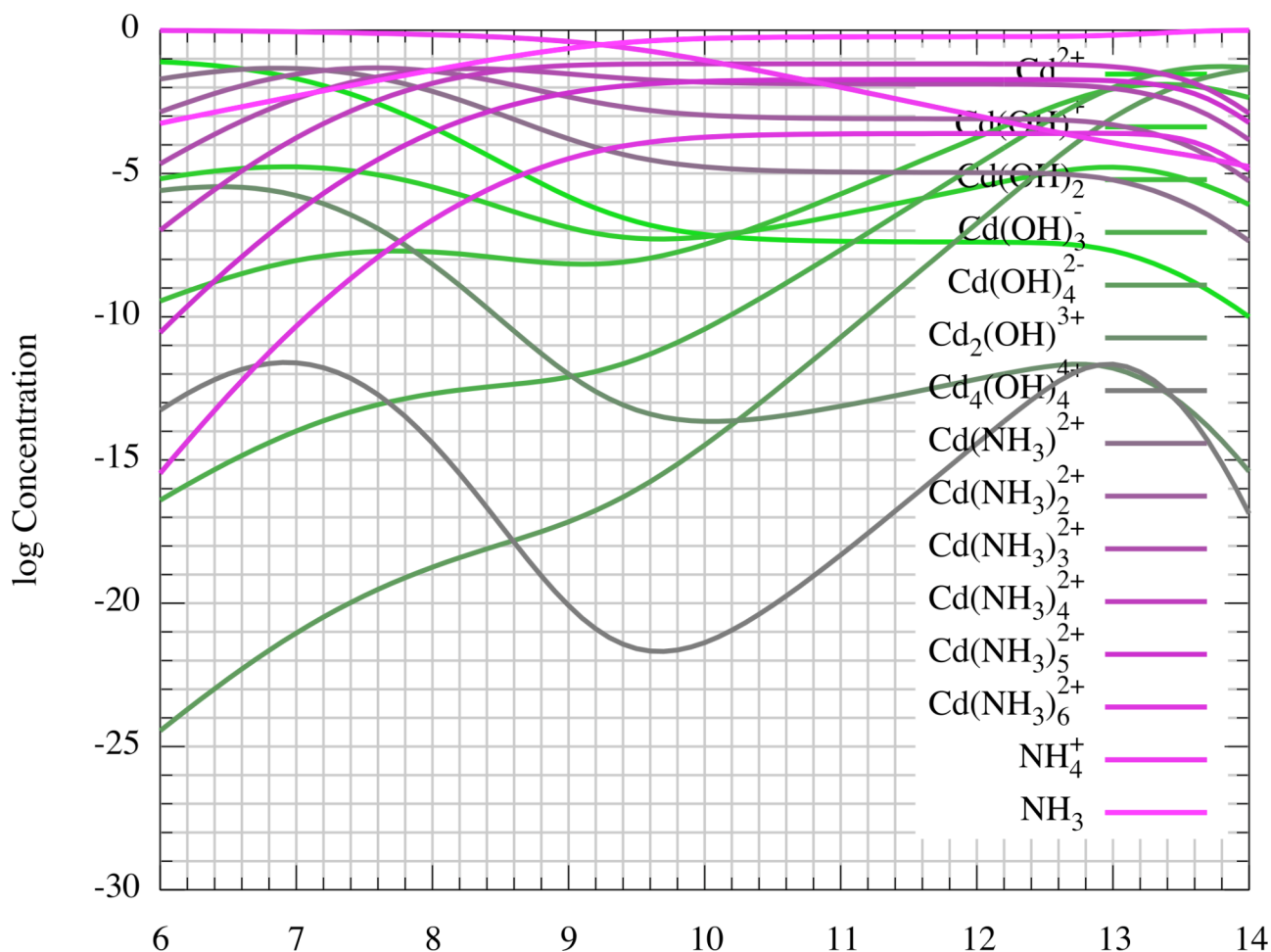
Figure 3 Complete speciation of 0.1 M cadmium in aqueous solution,

containing 1 M of ammonia, log molar concentrations versus pH.

Figure 3 shows the complete speciation of 0.1 M cadmium in aqueous solution with 1 M ammonium hydroxide and confirms the findings of Rieke and Bentjen [10]. The plot shows that near pH 6 Cd^{2+} is the major cadmium species. As the pH increases the concentration of NH_3 increases and so do the Cd ammonia complexes, resulting in a fall in $[Cd^{2+}]$, which remains fairly constant between pH 10 and 12.5. At pH above 13.5 the ammonia complexes hydrolyse to form hydroxides. The plateau of the $[Cd^{2+}]$ corresponds to the range where $[NH_3]$ becomes greater than $[NH4^+]$ and remains constant. However, the ideal pH value appears to be around 10 where Cd^{2+} is present in similar concentrations to $Cd(OH)^+$ and $Cd(OH)_2$.

A reduced plot in Figure 4 illustrates how the Cd^{2+} concentration is effectively regulated by the concentration of NH_3 and results in a plateau between pH 10.5 and 12.5.
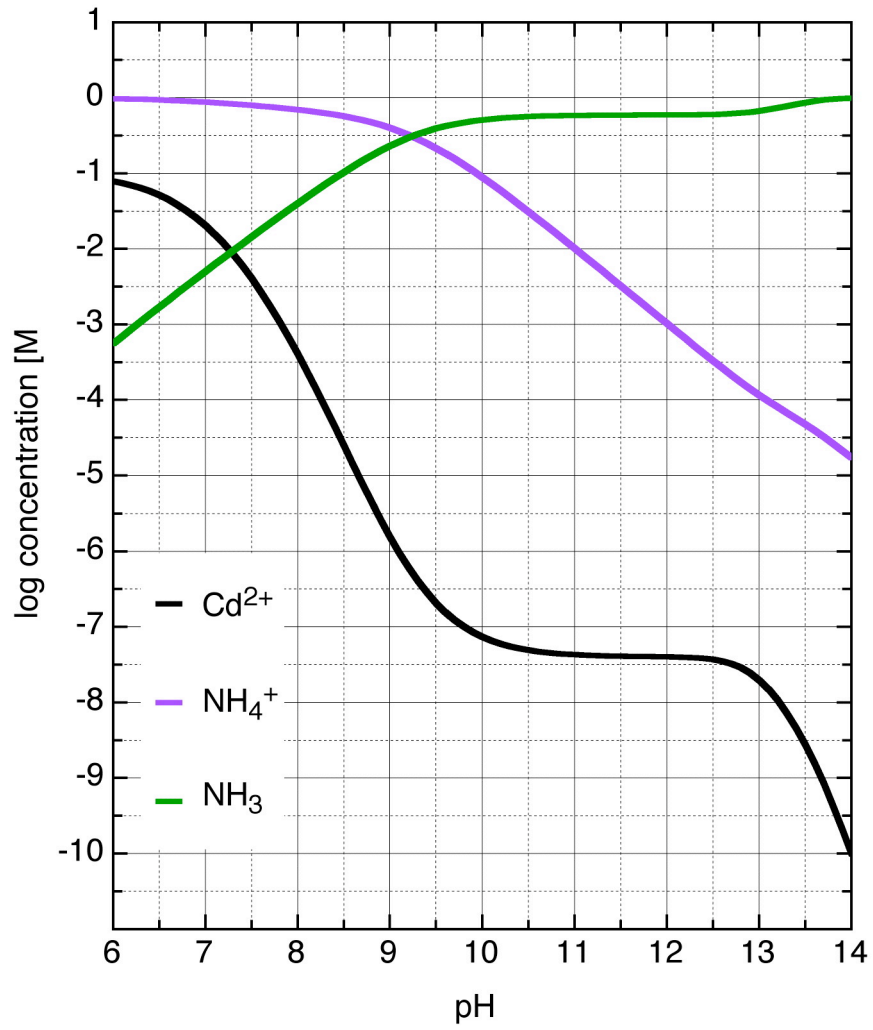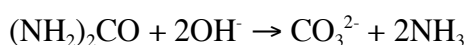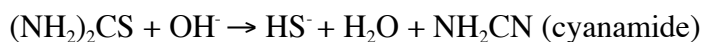
Figure 4 Concentration of Cd^{2+}, NH$_3$ and NH$_4^+$ species versus pH.

Thiourea hydrolysis

The sulphide ions could be added to the solution as sulphide salts such as sodium sulphide or through the hydrolysis of compounds such as thiourea or thioacetamide. The reactions below show the sequence in the hydrolysis in the NH_4OH at 60 °C of thiourea, with urea, ammonia and carbonate ions as by-products.

$(NH_2)_2CS + OH^- \rightarrow HS^- + H_2O + NH_2CN$ (cyanamide)

$NH_2CN + H_2O \rightarrow (NH_2)_2CO$

$NH_2CN + NH_4OH \rightarrow (H_2N)_2CNH_2^+$ (guanididium ion) $+ OH^-$

$(NH_2)_2CO + 2OH^- \rightarrow CO_3^{2-} + 2NH_3$

The equilibria of hydrogen sulphide can be calculated versus pH using the data in Table 3. The species present in solution are shown in Figure 5.

Table 3 Data used to calculate the speciation of hydrogen sulphide in aqueous solution [10]**.**

Reaction	Equilibrium constant
$H_2S \leftrightarrow HS^- + H^+$	pKS1 = 6.97
$HS^- \leftrightarrow S^{2-} + H^+$	pKS2 = 12.9
$H_2O \leftrightarrow OH^- + H^+$	logKw = -14
$Cd^{2+} + 2OH^- \leftrightarrow Cd(OH)_2(s)$	logKCd(OH)2 = -13.65
$Cd^{2+} + S^{2-} \leftrightarrow CdS(s)$	logKCdS = -26.1

The plot in Figure 5, calculated assuming a total sulphide concentration of 0.1 M indicates that the $[S^{2-}]$ is above 10^{-4} at the pH values used for bath deposition. Given that the solubility product of CdS is 10^{-26} it will always be supersaturated at the pH values under consideration.
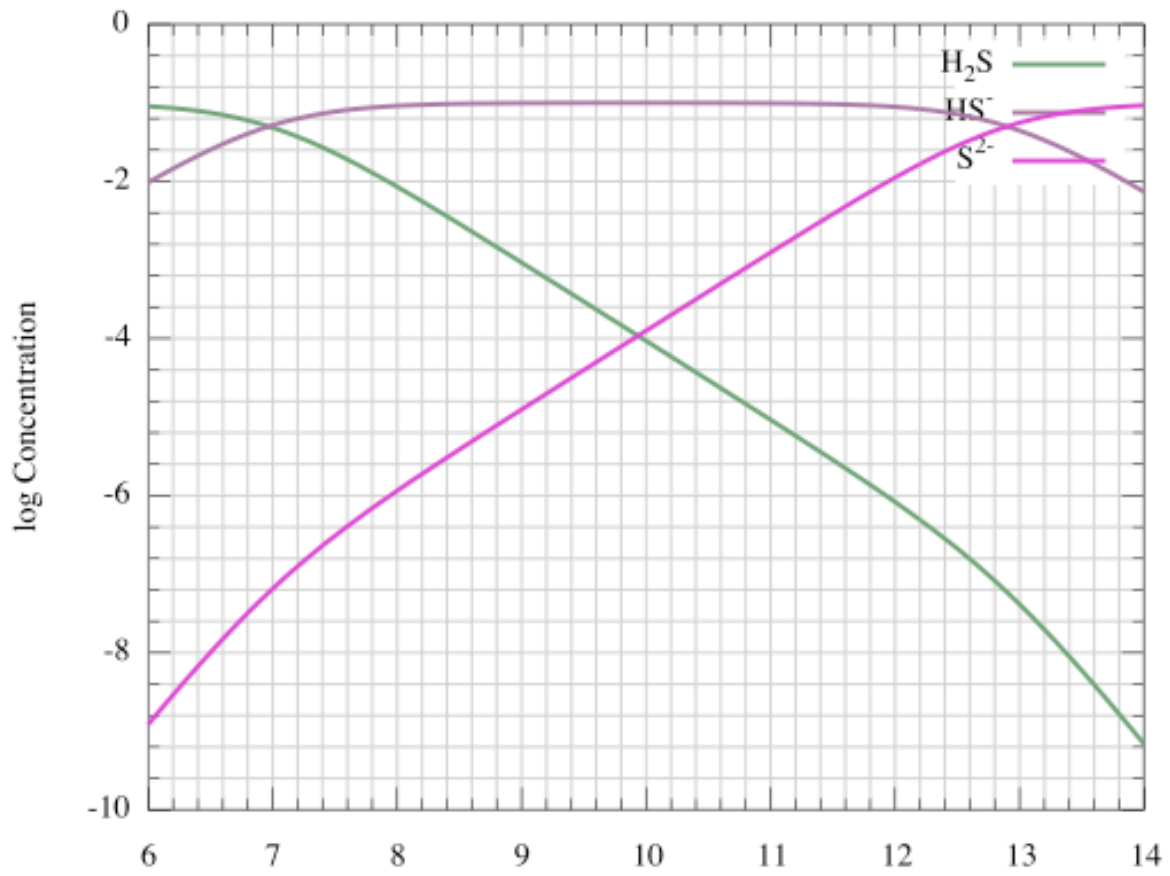
Sulphur species

Figure 5 Log concentration of sulphide species versus pH.

Electrodeposition

Electrodeposition is a widely used method for coating conducting substrates with metals, however, sulphides can be deposited using reactive solution containing sulphide ions. Various compound semiconductors have been deposited as films including ZnS [11, 12], CdS [13] and Cu_2ZnSnS_4 [14].

A review of the technique by Fulop and Taylor [15] describes the method for semiconductors. Electrodeposition can be performed from molten salts or from aqueous and or organic solutions. Cathodic or anodic deposition can be used but, in the case of CdS, cathodic deposition from dimethyl sulphoxide gave the best results [16-18]. Care must be taken in limiting the current densities to avoid cracking and adhesion improved if a little water was added to the solution. Pulsed electrodeposition can alleviate polarisation problems resulting in smoother films [12].

The simple set up in Figure 6 defines the electrolytic circuit. Usually galvanostatic (constant current at the working electrode or potentiostatic (constant potential between the working electrode and reference electrode methods are used as the power supply. These experiments are performed using a commercial potentiostat/galvanostat.
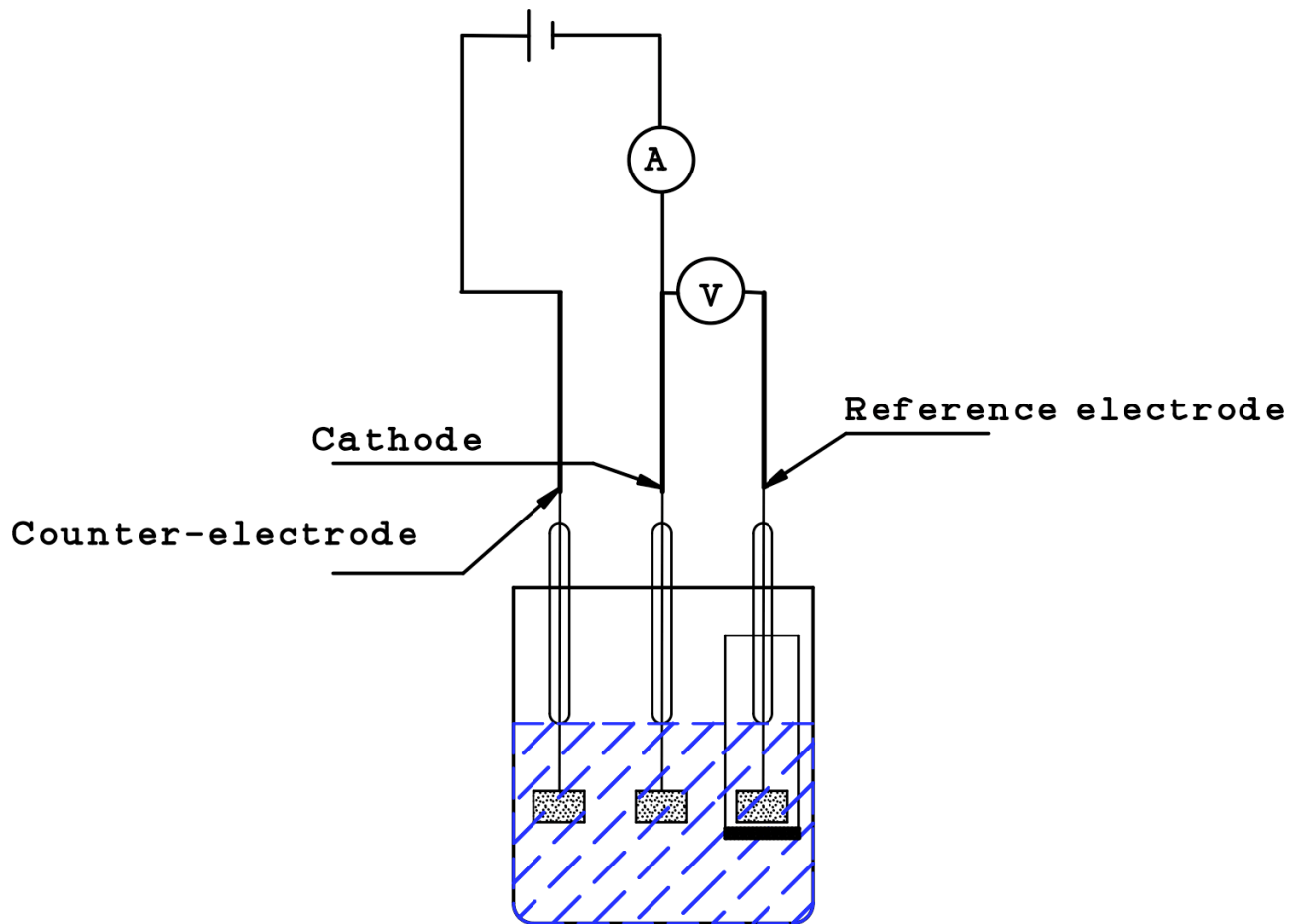
Figure 6 Simple three electrode apparatus for electrolytic deposition.

Conclusions

A brief review of solution deposition techniques for chalcogenides has been presented, both by chemical bath and electrodeposition.

A method of calculating speciation in CdS solutions has been developed using a free software package, Octave. The code also includes graphing of the data.

Solution deposition can be used successfully to grow films of chalcogenides both by coprecipitation and by electrodeposition. The low cost of the basic equipment makes it possible to perform basic experiments on the laboratory scale, moreover, the scalability of the technique makes these experiments relevant industrially.

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