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Developing an understanding of the processes controlling the chemical bath deposition of ZnS and CdS

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The deposition of cadmium sulfide by chemical bath methods is straightforward and involves an alkaline solution of a cadmium salt, a complexant and a chalcogen source, often thiourea or thioacetamide. Supersaturation of the bath with respect to '$Cd(OH)_2$' is necessary for the deposition of good quality films under a wide range of conditions. In contrast zinc sulfide is more difficult to deposit. In this paper we discuss the literature concerning the deposition of these chalcogenides and use equilibrium models to rationalise many of the observations found in the literature. Strategies for the deposition of high quality films of ZnS by CBD are discussed.

Introduction

There is considerable interest at present in the soft processing of materials.[1] Zinc and cadmium sulfide are compound semiconductors with a wide range of potential applications. These materials have many similarities, both exist in cubic or hexagonal forms and are wide-, direct-bandgap semiconductors.

The chemical bath deposition (CBD) process uses a controlled chemical reaction to effect the deposition of a thin film by precipitation. In a typical experiment substrates are immersed in an alkaline solution containing the chalcogenide source, the metal ion and added base. A chelating agent is also added to control the hydrolysis of the metal ion. The process relies on the slow release of S^{2-} ions into an alkaline solution in which the free metal ion is buffered at a low concentration. The speciation of metal ions, in particular the free metal ion concentration, is controlled by the formation of complex species, *e.g.* $[Zn(NH_3)_6]^{2+}$. The supply of sulfide ions is controlled by the decomposition of an organic sulfur containing compound, usually thiourea or thioacetamide. The solubility product of the compound in question helps maintain the stoichiometry of the deposited material, homogeneous compounds can be obtained as a result. A large number of physicochemical factors control the growth of the deposit under a specific set of reaction conditions. The supersaturation with respect to an individual phase is important as well as the kinetics of the growth processes. The technique has been used extensively to grow CdS and this is reflected in the numerous papers on the subject.[2–8] CBD is the production method for the CdS component of the 'Apollo' (CdS/CdTe) series solar cells manufactured by BP Solar. The deposition of ZnS by CBD is a more difficult proposition than that of CdS. In particular it is evident that there is a much wider range of conditions in which the concurrent deposition of zinc sulfide and oxide can occur.

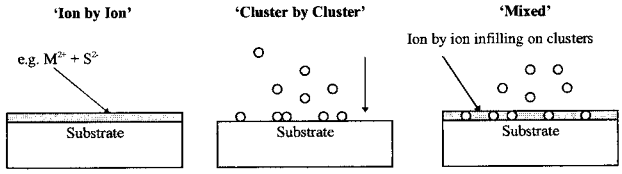
It would be useful to be able to deposit ZnS by CBD. There is a diverse range of applications for thin films of this semiconductor including as waveguides, heterojunction devices and in thin-film electroluminescent displays in which it is the most commonly used host material.[9] The potential of ZnS layers in blue light-emitting diodes (LEDs) and laser diodes is also an area which is well documented.[10] Applications in optoelectronic or photovoltaic devices is another area receiving attention, see for example Squeiros *et al.*,[11] but has yet to be fully developed. In CdS based solar cells, the use of wider bandgap materials such as ZnS or $Cd_xZn_{1-x}S$ could lead to decreases in window absorption losses and improvements in the short circuit current of the cells. Saitoh *et al.* have discussed the use of ZnS in passive structures such as optical waveguides,[12] while Landis *et al.*[13] have described the index-matching of wide-bandgap epitaxial heterojunction windows including ZnS for silicon based solar cells. On mercury cadmium telluride (HgCdTe), ZnS films can be used as gate dielectric layers in infrared photodetectors for CCDs[14] and hence have a potentially wide range of applications.

The CBD process

Film deposition

In chemical bath deposition experiments, solid material is formed which means that the bath must be thermodynamically unstable with respect to precipitation of the solid phase formed, *i.e.* supersaturated. There are two parent possible reactions leading to solid material, notably: (i) within the bulk of the solution (homogeneous precipitation); (ii) at a surface, the substrate or adventitious reaction on the reaction vessel surface (heterogeneous precipitation).

It is the second of these routes which leads to film formation. There is a tendency in the literature to discuss the deposition of thin films in terms of two distinct mechanisms or models. The models form end points in a complex series of potential processes for the deposition of adherent films encompassing many different possibilities (Fig. 1). The first of these is the



$M^{2+} + S^{2-} \rightarrow \text{'MS'}_{nuclei} \rightarrow \text{'MS'}_{particulate}$	ion by ion in solution, nucleation and growth
$M^{2+} + OH^- \rightarrow \text{'M(OH)}_2\text{'}_{nuclei} \rightarrow \text{'M(OH)}_2\text{'}_{particulate}$	ion by ion in solution, nucleation and growth of hydroxide
$\text{'M(OH)}_2\text{'}_{nuclei} + (NH_2)_2CS \rightarrow MS_{particulate}$	thiourea metathesis at surface of hydroxide
$\text{'MS'}_{nuclei} + (NH_2)_2CS + M^{2+} \rightarrow MS_{particulate}$	thiourea metathesis at surface of sulfide

Chemical Reactions

Fig. 1 Schematic representations of the processes which could lead to a thin film: ion-by-ion, cluster-by-cluster and mixed.

so-called ion-by-ion process in which the ions condense at the reacting surface to form the film. The second is termed the cluster-by-cluster process in which agglomeration of colloidal particles pre-formed in solution, by the homogeneous reaction, leads by absorption at the surface to particulate films. In practice both processes may occur and or interact, leading to films in which colloidal material is included in the growing films. The predominance of one mechanism over another is governed by the extent of heterogeneous and homogeneous nucleation. Key factors include the degree of supersaturation of the solution and the catalytic activity of the surface (substrate).[15] As indicated in (Fig. 1) there are several chemical reactions which can potentially be involved in each of these processes.

The mechanisms of CBD processes are really quite poorly understood and this is reflected in the literature. The actual processes leading to the formation of good quality adherent films are complex. The CdS system illustrates the point. Good quality (adherent) films are only obtained from baths which are supersaturated with respect to the precipitation of cadmium hydroxy species, irrespective of the substrate used. As the supersaturation of $Cd(OH)_n$ species is a very important factor in the formation of adherent films, the processes that might be important include: (i) the formation of clusters 'Cd_xOH_y'; (ii) the absorption of these 'nuclei' at the surface; (iii) the metathetical reactions of surface bound 'nuclei' with sulfide ions or thiourea in a heterogeneous process to form good quality CdS; and (iv) the formation and reactivity of pendant OH groups on the surface.

In early work, Kitaev *et al.* postulated[16] that the presence of hydroxide particles in solution was necessary for the growth of good quality films, the decomposition of thiourea being stimulated by a solid phase such as cadmium hydroxide. This proposal was supported by the observations of Kaur *et al.*[17] in that adherent films were only prepared in the presence of '$Cd(OH)_2$' in solution. The importance of '$Cd(OH)_2$' species in the growth mechanism of CdS even in conditions where no observable macroscopic precipitate is present is clear. Froment and Lincot[18] suggested that the mechanism of film formation, similar to that proposed by Parfitt,[19] could be represented by the following series of consecutive surface adsorption/reaction steps:

$$Cd^{2+}_{aq} + \text{site} + 2\ OH^- \rightarrow Cd(OH)_2\text{,ads} \qquad (1)$$

$$(NH_2)_2CS + Cd(OH)_2\text{,ads} \rightarrow C^* \qquad (2)$$

$$C^* \rightarrow CdS + \text{site} \qquad (3)$$

where C* is a reaction intermediate.

The supersaturation limit for the formation of '$Cd(OH)_2$' may be only coincidentaly signigficant as the pK_a of surface bound Cd^{2+} could be similar to that of the ion in solution. The formation of surface bound hydroxy species could be the important step which could serendipitously occur at a similar value of pH to the formation of a precipitate of the hydroxide.

Various other sequences of these reactions could lead to adherent CdS. It is interesting to note that freshly precipitated $Cd(OH)_2$ is readily metathesised to CdS in the presence of thiourea; this reaction appears not to happen with the zinc analogue. The solution species formed in the case of zinc are evidently different as is the degree of supersaturation.

CdS has been reported to grow epitaxially on single crystals by CBD such as InP.[20] This observation supports an ion-by-ion mechanism because of the register required between the substrate and growing layers at the atomic level. Further evidence comes from an HRTEM[18] study of material deposited before coalescence of the CdS film. Monocrystalline nuclei (30 nm) are formed at the substrate surface with the *c*-axis perpendicular to the surface. These crystallites coalesced to form a continuous film composed of microcrystallites (hexagonal, 20–80 nm).

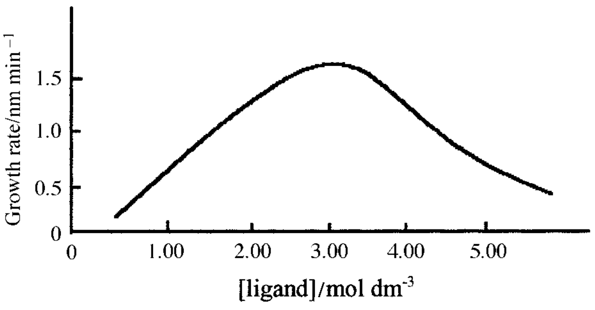


Fig. 2 Graph of growth rate *vs.* [ligand].

The situation is different for ZnS and Dona and Herrero[21] have suggested that as the growth rate for ZnS appeared be independent of stirring this allows the possibility of diffusion control to be discarded. They found that graphs of growth rate against $[NH_3]$ or $[N_2H_4]$ had similar profiles, see Fig. 2. There is an acceleration of growth rate with concentration up to an optimum concentration of the ligand (at molar concentrations, 1.5–2.0 nm min^{-1}) and then the rate rapidly declines. Similar relationships are observed for both complexing agents. Decreases in ligand concentration resulted in increases in the free zinc metal ion concentration and therefore an enhancement of homogeneous precipitation. Increases in concentration of either complexing ligand must reduce the amount of free zinc ion in solution and therefore restrict the growth rates of both homogeneous and heterogeneous precipitation.

Mokili *et al.*[22] have hence proposed that the formation of $Zn(OH)_2$ must be minimised in order to obtain ZnS due to possible competition between the formation of sulfide and hydroxide in basic solutions [$Zn(OH)_2$, $K_{sp} = 10^{-15.3}$ and ZnS, $K_{sp} = 10^{-23.8}$].

Froment and Lincot[18] found ZnS films to be different from those of CdS and to be an aggregation of spherical particles, in a more or less close packed structure. The distance between reticular planes revealed that the films were composed mainly of cubic ZnS. Electron diffraction patterns are similar to those for CdS colloids. Evidence like this indicates that the growth mechanism for ZnS is probably a colloid aggregation process. Similar findings have been reported by Mokili *et al.*,[22] TEM results revealing ZnS films composed of aggregated grains in an amorphous matrix.

In contrast, Dona and Herrero[21] suggest that the deposition process has its basis in the slow release of Zn^{2+} and S^{2-} ions in solution. These ions, it is suggested, condense on the substrates. This idea suggests an ion-by-ion process, opposing the statement of others. Contradictory statements such as these have prompted us to form the opinion that no proper, fundamental understanding of the process exists to date. Table 1 summarises some typical chemical bath conditions used in ZnS deposition.

Reaction kinetics

The kinetics of typical CBD processes (Fig. 3) appear to follow a sigmoidal profile similar to those observed for autocatalytic reactions.[23,24]

In solid state nucleation and growth processes, such reactions are often described by a formal kinetic expression such as the Avrami equation:

$$\alpha = 1 - e^{(-kt)} \qquad (4)$$

where α is the fractional decomposition, t the time and k a rate constant. This is an expression of the rate of formation of nuclei in the special case when there is completely random nucleation.[25] If we consider such processes in a qualitative way the kinetics are dominated by three phases: (i) initiation, often nucleation, the initial step usually requiring a high

Table 1 Some typical chemical bath conditions reported to have deposited ZnS

Counter ion, conc./M	Ligand 1, conc./M	Ligand 2, conc./M	Added base, conc./M	Sulfiding agent, conc./M	T/°C, growth rate/Å min^{-1}	Band gap/ eV	Phase reported	Ref.
sulfate, 0.14	NH_3, 3.75	HZ, 0.508	$Na_2B_4O_7$, 0.03	$(NH_2)_2CS$, 0.50	80, 10 90, 17			34
chloride, 0.20			NH_4^+/NH_3, 2.00	TAA, 0.04		3.60 n-type	cubic	15
chloride, 0.02				TAA, 0.02		4.10 >3.7	cubic	15
sulfate, 0.025	NH_3, 1.00	HZ, 3.00	$(NH_2)_2CS$, 0.035			3.76	cubic	16
sulfate, 0.05	TEA, 0.20		2.2 ml pH 10 NH_3/NH_4Cl	TAA, 0.04				17
sulfate, 0.05	TEA, 0.225			TAA, 0.02	17			19
sulfate, 0.025	NH_3, 1.00	HZ, 3.00		$(NH_2)_2CS$, 0.035		3.76	cubic	21
acetate, 0.001–0.01	HZ, 0.50–3.00		NH_4^+, 0.02	TAA, 0.001–0.1	<16.7	3.60–4.00		18
chloride, 0.075–0.190	HZ, 1.10			$(NH_2)_2CS$, 0.100–0.150	25, 1.5	3.85		22
chloride, 0.20	HZ, 4.00			$(NH_2)_2CS$, 0.20	16.7	3.70–3.80		42
acetate/sulfate, 0.025–0.050	HZ, 1.1–1.2	HZ, 3.00; en, 0.2; TEA, 0.07		$(NH_2)_2CS$, 0.035–0.1	25, 0.4			34

HZ, hydrazine (N_2H_4); TEA, triethanolamine; en, ethylenediamine; TAA, thioacetamide (CH_3CSNH_2). Glass substrates were used in all cases except ref. 17 where $CuInSe_2$ substrates were also used.

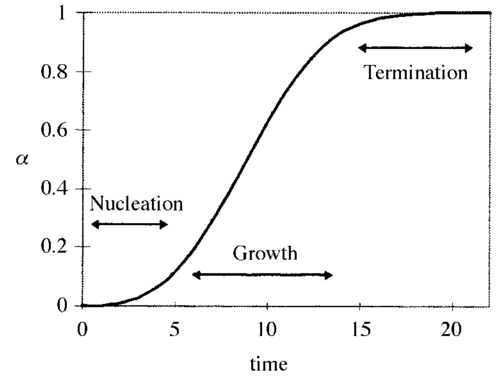


Fig. 3 Kinetic profile for a generalized autocatalytic process, fraction of reaction (α) *vs.* time.

activation energy in which reactive centres which catalyse the reaction are formed; (ii) the main phase of the reaction, sometimes zero order in which a number of reactive sites gives rise to a lower activation energy pathway, autocatalysis in a general sense, but in a heterogeneous reaction the growth of nuclei; and (iii) a termination step in which the reagent becomes depleted and the reaction begins to slow and eventually stops.

Intuitively this kind of general model is attractive for CBD processes and one thing which is interesting is that many CBD processes show a substantial linear portion in their kinetic profile (see for example ref. 18). This observation may suggest that in this phase of the reaction the process is controlled by a constant number of saturated reaction sites. There is an analogy here with the growth of thin films by MOCVD which is often arranged to be in a diffusion limited regime.

Equilibrium considerations

The metal ions zinc and cadmium are both labile, so it is reasonable to assume that in stirred solutions equilibria will be rapidly established, hence equilibrium models are useful in assessing the starting points of these chemically reactive baths. In any reaction which involves precipitation, the state of supersaturation of the system will be crucial and equilibrium calculations help to assess its extent. It is known in the deposition of CdS that the supersaturation of the reacting chemical bath with respect to hydroxy/oxy complexes of cadmium is extremely important in controlling the nature of the films deposited. There appears to be no such simple relationship for zinc sulfide deposition. The degrees of supersaturation in any system will depend on various factors including pH, ligand concentration and temperature.

It is interesting to compare the speciation in similar chemical baths for cadmium and zinc. If we take the ethylenediamine system as an example, a bath modestly supersaturated with respect to cadmium hydroxide is readily obtained at a 2:1 ligand to metal ratio ([Cd] = 180 mmol dm^{-3}, [en] = 360 mmol dm^{-3}), Fig. 4(a) pH > *ca.* 9.5. In contrast a similar

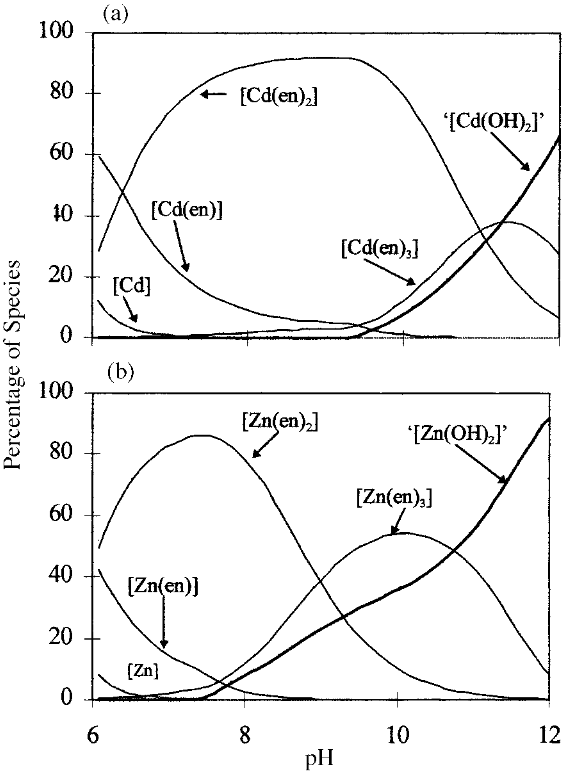


Fig. 4 Speciation diagram to illustrate the fundamental differences between cadmium and zinc complexation: (a) cadmium, (b) zinc. In each case [M] = 180 mmol dm^{-3} and [en] = 100 mmol dm^{-3} (equilibrium constant values are at 50 °C and from references 8 and 26).

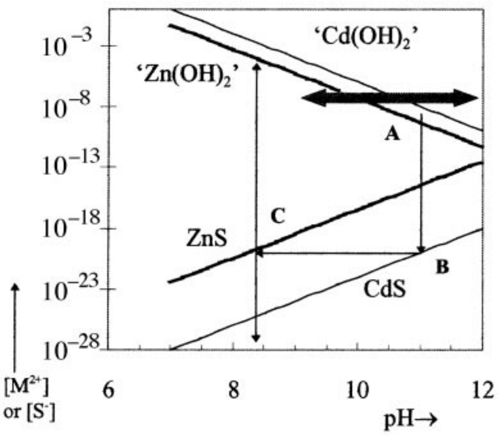


Fig. 5 Limiting solubility lines for '$M(OH)_2$' {[M]/mol dm^{-3} (for supersaturation) *vs.* pH, M = Cd or Zn} and corresponding supersaturation line ([S$^-$]/mol dm^{-3} *vs.* pH) [for illustration pK_{sp} values used at 20 °C: '$Zn(OH)_2$', 15.3; ZnS, 23.8; '$Cd(OH)_2$', 14; CdS, 28]. Double-headed arrow shows typical region used for CdS deposition, the path A to B to C is explained in the text.

bath containing zinc is unstable with respect to precipitation of the hydroxide at much lower values of pH > *ca.* 7.5. In the presence of modest amounts of a sulfiding agent, in the alkaline region, the cadmium bath deposits CdS while in the corresponding zinc bath ZnO/hydroxide is more easily formed.

The above calulations draw attention to a fact that we and others have commented on in several papers, *i.e.* the importance of the supersaturation of cadmium solutions with respect to hydroxy species as a necessary condition for the growth of good quality films of CdS. It is possible to further develop this approach in a comparative way by considering the solubility limits for metal hydroxy species as a function of pH. At any value of pH there is a limiting value of pM (defined by $K_{spOH_2}/[OH]^2$) below which supersaturation will occur. These limits are approximately linear on plots of pM *vs.* pH, Fig. 5. At pH 10–11, we know good quality CdS would be deposited from such a solution. This condition is sufficient to define a minimum sulfide ion concentration at which metathesis to the sulfide becomes a preferred reaction ($K_{spS}/[M]$). It is striking that CdS is much more stable than ZnS and this is again graphically illustrated (Fig. 5). The actual supersaturation in a reactive chemical bath will depend on the sulfide ion concentration, however the relative positions of the lines for cadmium and zinc will be unchanged.

If we assume that as CdS and ZnS are similar materials (structurally), a similar path is in principle possible for their deposition as thin films. We can investigate this idea by defining equivalent conditions for ZnS and CdS in terms of supersaturation for the sulfide, which are found by following the line B–C on Fig. 5.

There are several important conclusions that we can draw from this simple calculation: (i) equivalent levels of supersaturation for the sulfide are found at pH values *ca.* 2.5 lower for ZnS than CdS; (ii) if reactions are carried out in a high pH regime more sulfiding agent (by *ca.* 4 orders of magnitude!) will be needed for the zinc system, even so the degree of supersaturation for zinc with respect to the hydroxide will always be greater than for cadmium with respect to its hydroxide (values of pM and pH being equal); and (iii) at lower pH the rate of hydrolysis of the sulfide source is likely to be lower so again even if a lower pH is used more sulfide source will be needed.

It is interesting to note that an intuitive attempt to develop this kind of approach has been reported.[27] The chemical bath used contained zinc ions and urea, at modestly acid values of pH. The urea slowly hydrolysed in the bath to provide hydroxide and thioacetamide hydrolysed as the hydroxide was released. In a typical deposition experiment (90 °C, 1 h), a conformal film *ca.* 0.6 μm thick was deposited. It would be interesting to look at the possibility for ternary material deposition from such baths which operate at much lower pH values than are typical for CBD. The films deposited by this method had bandgaps close to that expected for ZnS.

Nature of the films deposited in ZnS experiments

Electronic properties. Another important issue concerns the bandgaps of films deposited from ammonia free baths discussed above[27] which are close to that expected for bulk ZnS (3.6 eV). Films deposited from ammonia containing baths have been reported to have bandgaps (4.1–3.9 eV) consistently higher than the bulk value,[28] Table 1. There has been speculation that this effect is due to quantum confinement in the very small (grain size 3–6 nm) crystallites of which these films were composed.[29] In essence, a 3-D quantum size effect is suggested to be occurring in which electrons are localised in individual crystallites of polycrystalline thin films.[30] CdSe films have been grown where bandgap values were apparently up to 0.5 eV higher than in single-crystal samples.[31] Similar observations relate to PbSe films[32] which were found to contain crystals of varying size depending on the deposition parameters, in particular the nature of the complexing agent, the film thickness and the deposition temperature, and ZnS particulate films (particle size 30–60 Å).[33] Although such effects have been explained by quantum confinement, it is entirely possible that some of the films are chemically inhomogeneous with a significant quantity of oxide/hydroxide incorporation.

Film composition. Many of the films reported as ZnS which have not been rigorously characterised are probably at best heavily contaminated with zinc oxide or hydroxide. In an RBS study Mokili *et al.*[22] showed that CBD deposits contained significant amounts of oxygen. EXAFS confirmed the presence of oxygen in the form of hydroxide and a high oxygen to sulfur ratio was found. The compositions of some films were even reported to be close to $Zn(OH)_2$. In more basic solutions containing hydrazine, deposits of material close in stoichiometry to ZnS were obtained, but even such samples were not of the pure sulfide and were contaminated with either oxide ($ZnO_{0.5}S_{0.5}$) or hydroxide [$Zn(OH)S_{0.5}$].

On the basis of these studies they proposed a deposition mechanism involving hydroxide intermediates and suggested that if the transformation of hydroxide into sulfide is too slow, significant amounts of hydroxide would be present in the final film. A general conclusion is that the presence of a significant quantity of oxide or hydroxide in the ZnS films may be explained by the proximity of the solubility lines of the sulfide and the hydroxide.

Later EXAFS studies by Mokili *et al.*[34] showed that thin films prepared by CBD in alkaline ammonia solutions containing a zinc salt, thiourea and different amine additives were zinc hydroxosulfide, the oxygen content of which ranged between 39 and 82%. FTIR studies supported the evidence suggesting that the films consisted mainly of $Zn(OH)_2$ with little or no ZnO present. A clear absorption at 648 cm^{-1} was assigned to a Zn—OH stretching mode by Kauffman *et al.*[35] The Zn—O bond peak position (at 430 cm^{-1} from a ZnO powder sample) was very weak in most spectra thus rejecting the hypothesis that significant amounts of ZnO were formed in the films. Such compositions were present even without post-annealing.

A point worth stressing is the similarity of the conditions used in the Mokili study[34] to those used in the majority of the other studies of ZnS by CBD, Table 1. All of the reported conditions for the deposition of ZnS as detailed in Table 1 are remarkably similar and suggest that there is the distinct possibility of heavy oxide contamination or incorporation in many of the films reported as ZnS.

The chemistry of sulfide delivery

In essence, the chemistry involved in the CBD of ZnS is straightforward. Thiourea decomposition will occur in CBD baths essentially as described in the kinetics studies carried out by Marcotrigiano *et al.*[36] into the desulfuration of thiourea in sodium hydroxide. They postulated that in alkaline solutions, thiourea first gives sodium sulfide and cyanamide which is then transformed into cyanamide, amidinourea, guanidine or, at pH 12, almost quantitatively into urea which isomerizes to ammonium cyanate and is finally hydrolysed to ammonium carbonate:

$$(NH_2)_2CS + OH^- \rightarrow NCNH_2 + SH^- + H_2O \qquad (5)$$

$$NCNH_2 + H_2O \rightarrow O{=}C(NH_2)_2 \qquad (6)$$

$$O{=}C(NH_2)_2 \rightarrow NH_4CNO \qquad (7)$$

$$OCN^- + 2\ H_2O \rightarrow HCO_3{}^- + NH_3 \qquad (8)$$

The cyanate and carbonate ion are thought to form very early in the reaction and may be responsible for the hydroxide consumption being greater than that corresponding to reaction (2). It is assumed that the hydroxide consumption equals the SH^- formation. It is known that thiourea behaves as a zwitterion[37] which may play a role in the thiourea desulfuration. Recent observations in our laboratory may suggest that under typical CBD conditions, decomposition of thiourea proceeds only as far as urea.

Strategies for growth

The fact that the CBD of CdS produces highly crystalline, conformal, adherent films relatively easily suggests that one strategy for growing good films of ZnS would be to alter the bath conditions to favour the same mechanism that governs CdS deposition. Froment and Lincot[18] suggested that by changing the composition of the reacting solutions competition between the processes of homogeneous and heterogeneous nucleation could be altered to favour thin film growth. Subsequent experimental work by Mokili in conjunction with Froment and Lincot,[22] however, has shown that no marked changes with regards to the growth curves occurred for ZnS when the conditions approached and/or crossed the precipitation lines. This behaviour is quite unlike that of the cadmium sulfide systems for which a clear change in the growth habitat is observed when supersaturation is achieved.[38] They have also suggested that there is little or no induction time associated with ZnS growth which may suggest that growth depends on colloidal material in this case.

Gorer and Hodes[39] suggested for CdSe that the presence or absence of hydroxide particulate material in solution may govern the transition between atom-by-atom and colloidal growth. The change in mechanism was apparently indicated by a sharp change in crystal size (observed by shifts from blue to red in optical spectra). They suggested a 'critical ratio' R(c) (concentration of complexing agent, nitrilotriacetate, to cadmium salt) below which $Cd(OH)_2$ was present and above which it was not, despite a visible $Cd(OH)_2$ suspension under any condition. This led them to propose that below R(c) the mechanism is initiated on the $Cd(OH)_2$ colloidal particles adsorbed on the substrate and above R(c), deposition occurs directly on the substrate by initial film formation without $Cd(OH)_2$.

However, it is hard to justify the importance of a critical ratio of metal to ligand. We have defined a useful concept of equivalence in terms of a contour defining a constant value of pM on a plot of total metal ion concentration against total ligand concentration.[40] The use of such plots has enabled us to predict for the CdS system the composition of baths which will produce high quality films at different concentrations or how the substitution of one ligand with another, *e.g.* ethylenediamine for ammonia, can be made in such a way as to maintain good quality film deposition. A typical plot is shown in Fig. 6 for the ethylenediamine cadmium system. The contour defining constant pM is a curve and much higher ratios of ligand to metal are needed as the overall concentration decreases. This idea is consistent with the tendency of complexes to dissociate on dilution. The third line shows the contour for a constant ligand to metal ratio of 3:1 which emphasises that this line is different from that defining a constant pM. There will of course be a critical ratio if one of the variables is held constant as can be seen from Fig. 6 and the concept is useful at high concentration, but this idea does not allow for the method to be generalised.

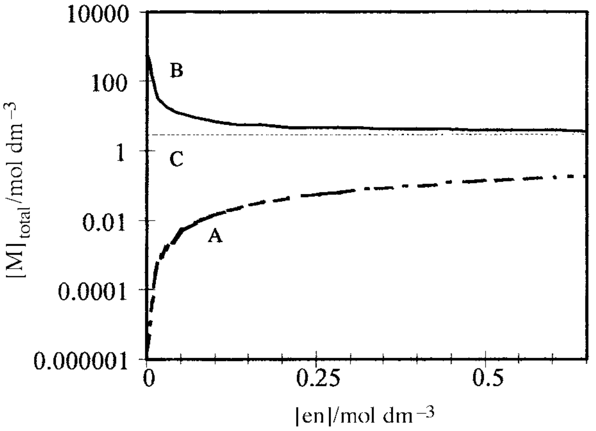


Fig. 6 Equivalent solutions. (A) An equivalent solution contour plot for pM = 9 ($[M]_{total}$ *vs.* $[en]_{total}$) for the cadmium ethylenediamine system at 50 °C (see ref. 8 for relevant constants); (B) $[en]_{total}/[M]_{total}$ for pM = 9, (C) $[en]/[M]_{total} = 3$. (valid for $pH \gg pK_{a2}$ of ethylenediamine).

In related work on PbSe Gorer *et al.*[41] appear to support the possibility of a mechanism crossover. Experimental conditions were demonstrated where either one or both growth mechanisms could lead to fine control of the film properties.

Conclusions understanding ZnS deposition in relation to physico-chemistry

The use of a second ligand

Many workers report the use of a second ligand in the chemical bath when attempting the deposition of ZnS. Hydrazine is a popular choice in the CBD of ZnS. A typical observation is that of Ortega-Borges *et al.*[27] who reported that the use of ammonia and thiourea without hydrazine resulted in films which were not homogeneous or adherent.

In a related observation Dona and Herrero[21] have suggested that the addition of hydrazine, 'although not essential, improves homogeneity, specularity and growth rate'. Ndukwe also used hydrazine.[42] Dona and Herrero have suggested that the rate-determining step for the heterogeneous process may involve the dissociation of a $Zn^{2+}-L$ bond. This suggestion is unlikely as zinc is classically a labile metal ion. Another possibility is that the hydrazine complex ions have a lower coordination number (and therefore less steric impediment for the approach of the sulfide ion). Hydrazine could potentially act as a bridging ligand and perhaps facilitate surface binding. One thing which must be noted is that at a constant pH the addition of a second ligand can only lead to a lowering of the free metal ion concentration. In the case of zinc this will lower supersaturation with respect to either oxide/hydroxide phases or the sulfide.

The most detailed investigation into the addition of amines has been carried out by Mokili *et al.*[22] They found that, in all cases, the addition of either hydrazine, triethanolamine or ethanolamine to ammonia increased thin film growth rates. Using hydrazine, a maximum growth rate (increased by a factor of four) could be achieved at 3 mol dm^{-3}. However, they suggest that hydrazine accelerates the hydrolysis of thiourea. Other amines tended to increase the growth rate but did not change significantly the speciation in the bath (precipitation line, pH, *etc.*). Hence for hydrazine and triethanolamine they proposed that these molecules participated in the decomposition of thiourea.

Dona and Herrero reached similar conclusions[21] and have speculated that the relationship between complexing agents and growth rates are typical of a system which has 'two competing processes' namely heterogeneous and homogeneous precipitation. They also consider the heterogeneous process to be 'limited by complex ion adsorbability' and by 'the adsorption points on the substrate'. In considering the possibility that the effect of additional amines is primarily on the sulfiding agent Ortega-Borges *et al.*[27] have developed an essentially ligand free system, *vide supra*.

Important factors

CBD is potentially a method for the deposition of thin films of ZnS. It is also a method free of the many inherent problems associated with high temperature techniques such as MOCVD including increased point defect concentration, evaporation of ZnS leading to polysulfide and a limited choice of substrate. However to date only a small number of papers have reported on the deposition of ZnS, by the CBD method, in any detail. At present progress may be limited by a poor appreciation of the complexity of the system and a more thorough understanding of the underlying mechanism involved is required for the design of better deposition systems.

In conclusion there are a number of fundamental differences between the CdS and ZnS systems which need to be appreciated: (i) CdS must, in some cases, be deposited by a mechanism operating at close to the atomic level; epitaxy can be observed. The deposition of ZnS is often different and involves clusters of ZnS. Part of the challenge in developing the deposition of ZnS and related ternaries is to drive the process toward a surface controlled ion-by-ion process. (ii) The effect of pH in the CdS system is to form $Cd_x(OH)_y$ species; those crucial for film growth are bound to the surface of the substrate. These metathesise to the sulfide. In the ZnS system high pH tends to lead to the formation of $Zn(OH)_2/ZnO$ either on the surface or as bulk material. At high values of pH metathesis of these compounds to the sulfide is much less favourable than for the cadmium species which can be rationalised by the relatively small differences in the solubility products for ZnS ($pK_{sp}=24$ at 25 °C) and $ZnO/Zn(OH)_2$ ($pK_{sp}=17$ at 25 °C). (iii) The deposition of good quality ZnS appears to be optimal in the presence of two complexants, typically ammonia and hydrazine. The dominant advantageous effect of the second ligand may be to enhance the rate of decomposition of thiourea increasing the rate of sulfidization of the growing film. (iv) In many cases there is the possibility that the literature does not strictly report ZnS growth but more accurately a zinc hydroxysulfide material.

We consider that a more closely controlled growth environment is a necessity if substantial advances in this field are to be made.

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