

Thermodynamic Analysis of the Deposition of Zinc Oxide and Chalcogenides from Aqueous Solutions

Antonio M. Chaparro*

CIEMAT, Avda. Complutense, 22, 28040-Madrid, Spain

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The synthesis of zinc oxide and chalcogenides from aqueous solution is analyzed from a thermodynamic point of view. The study is intended to explain the results of recipes normally used for the growth of thin films of zinc oxide and chalcogenides from chemical solutions. Different reaction possibilities are compared in a solution of zinc, ammonia as complexant, chalcogenide anions, and hydrazine. The composition of the solution is analyzed by means of thermodynamic diagrams, as a function of pH, ammonia concentration, and redox potential. The reactivity in the solution is discussed, and free energy changes are compared as a function of pH for the different possible reactions. It arises that ZnO growth by an electroless–chemical process is the most favored reaction in nonde-aerated solutions. This reaction consists of the reduction of naturally dissolved oxygen by the chalcogenide anion, or other added reducer (hydrazine), followed by chemical formation of ZnO. Zinc chalcogenides appear to be metastable phases in the aerated solutions. Under anoxic conditions, the chalcogenides are stable phases, and the most favored process (i.e., with highest free energy change) is found to be induced by hydrazine oxidation and proton reduction. That explains experimental observations that show that hydrazine is always necessary to obtain zinc chalcogenide thin films from solution deposition. In the absence of hydrazine, the oxidation of the chalcogenide is the preferential reaction, and a film with mixed composition is obtained. On the other hand, the pure chemical precipitation, usually considered as to be responsible for chalcogenide deposition from solution, is a less favored reaction and probably plays a minor role. As for ZnTe solution deposition, the high reducing character of telluride makes it impossible to obtain pure ZnTe films but gives either a mixture of ZnO and Te or ZnTe and Te depending on conditions in the solution.

Introduction

Zinc oxide (ZnO) and chalcogenides (ZnX) are semiconductor compounds with a large role in photovoltaics, photochemistry, photonics (laser), sensors, and nano-electronics. They can be grown as thin films by different techniques, such as molecular beam epitaxy, chemical vapor deposition, sputtering, or metal–organic vapor deposition, as well as low-temperature ambient pressure methods, such as electrochemical,^{1–5} electroless,^{6,7} sol–gel,⁸ and solution deposition.^{9–11} These methods are usually considered soft (low temperature, ambient pressure, chemical interactions)

and are found to be most appropriate when the alteration of the substrate must be avoided or limited to the surface, for instance, to generate a buffer film on a photoactive material like the absorber of a solar cell.¹² Among aqueous solution methods, electroless and chemical deposition are the most simple because they only rely on the composition and temperature of a chemical bath. The conditions for the growth of adherent films can be found from several works, although the process is usually poorly understood, and great difficulty and controversy are found to explain aspects such as the role of the different reactants added in the bath, the reactions occurring for the growth of the film, or the properties of the resulting films. For zinc chalcogenide synthesis, the solution usually includes a zinc salt, ammonia, hydrazine, and a chalcogen precursor.^{13–21} The slow and progressive precipi-

* Corresponding author. Phone: 34 913466622; fax: 34 913466037; e-mail: antonio.mchaparro@ciemat.es.

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tation of the chalcogenide in this solution is considered to be the process that generates the compound and the film. However, this reaction alone does not explain experimental observations, such as the role of hydrazine, the high proportion of zinc oxide and chalcogen in different oxidation states (Se^0 , SO_4^{2-}) in the films, or the growth kinetics observed.²²

One principal aspect usually not considered is the different reaction possibilities in the solution. For instance, the chalcogenide anion itself ($\text{X}^{2-} = \text{S}^{2-}$, Se^{2-} , Te^{2-}) may participate as a reducer (reaction 1) and as zinc precipitant (reaction 2)



(solid compounds bolded). Reactivity is further complicated by other reactants present intentionally or unintentionally in the solution. Hydrazine (N_2H_4) is included in most recipes to obtain films with good quality,¹³ but its role is controversial, and different explanations can be found in the literature^{13,14,16,20} that consider it either a second complexant for zinc or a reducer. On the other hand, naturally dissolved oxygen is present in significant concentrations ($[\text{O}_2] \approx 10^{-3}$ to 10^{-4} M in the 0–100 °C temperature range²²) in nondeaerated solutions employed in most cases, in which contribution to the growth of the film may be important. For instance, the reaction of oxygen with a reducer in the presence of zinc cations is favored, kinetically and thermodynamically, for the formation of ZnO .⁶ Solvent species (OH^- , H^+) may also participate in the deposition of the compounds under certain conditions, via precipitation or electrochemical reaction, as described below. As a consequence of the different reaction possibilities, the properties of the resulting films may be loosely controlled, usually showing variable structure, morphology, and composition. It is therefore of interest to analyze the reaction possibilities, their characteristics, and their importance to help in the optimization of solution growth of zinc compound thin films.

Understanding the reactivity of such complex aqueous systems should depart from the analysis of the thermodynamic data. Such analysis, involving many variables and reaction possibilities, is better carried out by means of diagrams showing equilibrium concentration of the different species, predominant species, and redox reactivity (Pourbaix diagrams).^{23,24} The diagrams give a comprehensive picture of the solution under different conditions of pH, redox potential, and/or concentrations and allow us to predict possible reactions. The thermodynamic analysis presented here applies to an aqueous solution typically used for the

Table 1. Normal Potentials (25 °C) for the Electrochemical Reactions^a

| no. | reaction | E° (V) |
|-----|--|---------------|
| 1 | $\text{H}^+ + \text{e}^- \rightarrow \text{H}_2$ | 0.0 |
| 2 | $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}^0$ | -0.762 |
| 3 | $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ | 1.23 |
| 4 | $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$ | 0.68 |
| 5 | $\text{N}_2 + 4\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{N}_2\text{H}_4 + 4\text{OH}^-$ | -1.15 |
| 6 | $\text{S}^0 + 2\text{e}^- \rightarrow \text{S}^{2-}$ | -0.476 |
| 7 | $\text{Se}^0 + 2\text{e}^- \rightarrow \text{Se}^{2-}$ | -0.924 |
| 8 | $\text{Te}^0 + 2\text{e}^- \rightarrow \text{Te}^{2-}$ | -1.143 |
| 9 | $\text{Zn}^{2+} + 0.5\text{O}_2 + 2\text{e}^- \rightarrow \text{ZnO}$ | 0.88 |
| 10 | $\text{Zn}^{2+} + \text{S}^0 + 2\text{e}^- \rightarrow \text{ZnS}$ | 0.28 |
| 11 | $\text{Zn}^{2+} + \text{Se}^0 + 2\text{e}^- \rightarrow \text{ZnSe}$ | 0.08 |
| 12 | $\text{Zn}^{2+} + \text{Te}^0 + 2\text{e}^- \rightarrow \text{ZnTe}$ | -0.03 |
| 13 | $\text{ZnO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{Zn}^0 + \text{H}_2\text{O}$ | -0.41 |
| 14 | $\text{ZnS} + 2\text{e}^- \rightarrow \text{Zn}^0 + \text{S}^{2-}$ | -1.52 |
| 15 | $\text{ZnSe} + 2\text{e}^- \rightarrow \text{Zn}^0 + \text{Se}^{2-}$ | -1.77 |
| 16 | $\text{ZnTe} + 2\text{e}^- \rightarrow \text{Zn}^0 + \text{Te}^{2-}$ | -1.82 |

^a Bold = solid compounds and italics = calculated values.

Table 2. Free Energies of Formation and Solubility Constants for Zinc Compounds (25 °C)

| | $-\Delta G_f^\circ$ (kJ mol ⁻¹) | $\text{p}K_s$ |
|---------------------------------|---|---------------|
| ZnO | 317 | 11.2 |
| ϵ -Zn(OH) ₂ | 556 | 14.8 |
| ZnS (sphalerite) | 201.1 | 24.7 |
| ZnSe | 163 | 26.4 |
| ZnTe | 141.6 | 25.2 |

Table 3. Dissociation Constants for Complexes and Acid/Base Constants (25 °C)

| | | x | | | |
|---------------|---|------|-----|-----|-----|
| | | 1 | 2 | 3 | 4 |
| $\text{p}K_d$ | $\text{Zn}(\text{NH}_3)_x^{2+}$ | 2.2 | 4.5 | 6.9 | 9.6 |
| $\text{p}K_d$ | $\text{Zn}(\text{N}_2\text{H}_6)_x^{2+}$ | 2.4 | 4.2 | 5.5 | |
| $\text{p}K_a$ | $\text{NH}_3 + x/\text{NH}_3$ | 9.3 | | | |
| $\text{p}K_a$ | $\text{N}_2\text{H}_4 + x/\text{N}_2\text{H}_4$ | 8.1 | | | |
| $\text{p}K_a$ | $\text{SH}_x^{x-2}/\text{SH}_{x-1}^{x-3}$ | 13.9 | 7.0 | | |
| $\text{p}K_a$ | $\text{SeH}_x^{x-2}/\text{SeH}_{x-1}^{x-3}$ | 14.0 | 3.7 | | |
| $\text{p}K_a$ | $\text{TeH}_x^{x-2}/\text{TeH}_{x-1}^{x-3}$ | 11.0 | 2.7 | | |

deposition of zinc chalcogenides, including zinc cations in the presence of complexing NH_3 and chalcogenide anions. The role of other additives such as hydrazine and molecular oxygen is also analyzed. For completeness, the study also includes the possibility of ZnTe deposition.

Characterization of the Solutions from Thermodynamic Diagrams

The diagrams apply to aqueous solutions of zinc cations, together with ammonia, hydrazine, the chalcogen anions, and dissolved oxygen (1 atm partial pressure), at 25 °C and concentrations usually employed in most studies. In fact, the chalcogen anion is not added directly but appears in the solution as a result of the decomposition of a precursor (thiourea, selenourea, selenosulfite, etc.),^{9,10} although this fact does not affect the generality of the analysis. The data used for the calculation of the diagrams, extracted from different sources,^{25–27} are given in Tables 1–3. The logarithmic concentration of the zinc species in aqueous solution is shown

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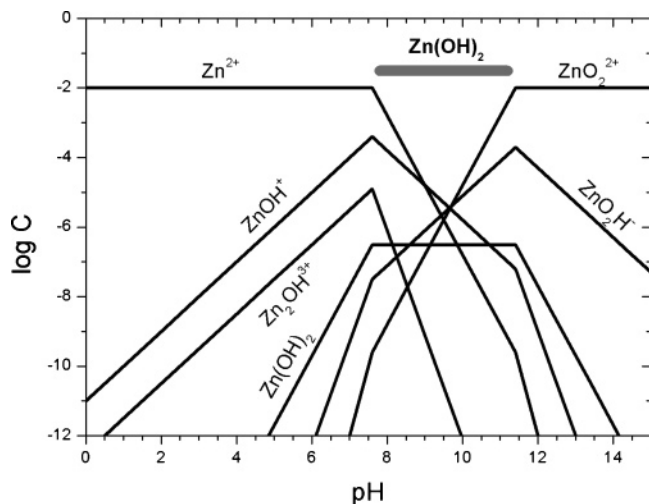


Figure 1. Log(C)–pH diagram of zinc(II) 10^{-2} M.

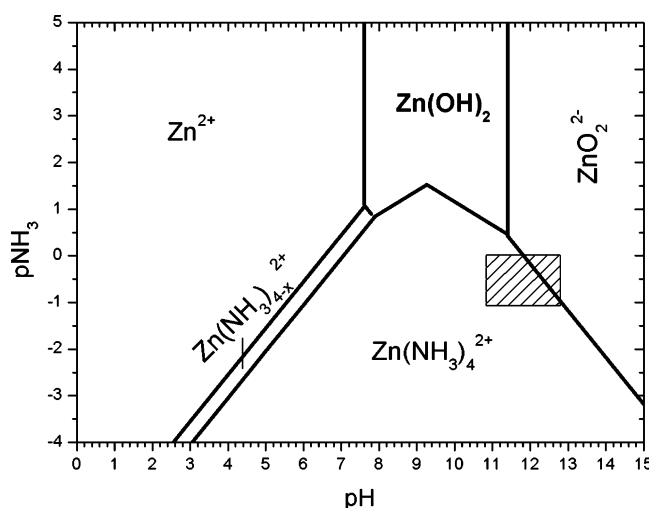


Figure 2. $p\text{NH}_3$ –pH diagram of zinc (II) 10^{-2} M. The dashed area corresponds to the conditions mostly employed for solution deposition of zinc compounds.

in the diagram of Figure 1. Three predominant Zn (II) species must be considered, namely, Zn^{2+} ($\text{pH} < 7.6$), $\text{Zn}(\text{OH})_2$ ($7.6 < \text{pH} < 11.4$), and ZnO_2^{2-} ($\text{pH} > 11.4$). The precipitation of $\text{Zn}(\text{OH})_2$ is avoided by using a complexing agent that maintains zinc dissolved in the widest pH range.²⁶ The analysis here restricts to ammonia as complexing agent, which is most used for deposition of Zn(II) chalcogenides because it forms complexes of medium stability, allows for the complete dissolution of zinc, establishes an appropriate basic pH for the decomposition of chalcogenide precursors, and has high stability in the solution. Figure 2 shows the predominance species diagram $p\text{NH}_3$ –pH for zinc, constructed from Figure 1 and introducing the acid–base equilibrium of NH_3 . This type of diagram is divided in areas of predominant species separated by lines of coexistence; 0.3 logarithmic units away from a line inside a predominance area corresponds to 90% concentration of the predominant species. The diagram in Figure 2 shows that NH_3 concentrations above 0.3 M allow us to maintain zinc (10^{-2} M) in dissolution at any pH in the form of different species, namely, Zn^{2+} , $\text{Zn}(\text{NH}_3)_x^{2+}$ ($x = 1, 2, 3$), $\text{Zn}(\text{NH}_3)_4^{2+}$, and ZnO_2^{2-} . Predominance diagrams of interest to follow the chemical deposition of chalcogenides (ZnX) are of the type $p\text{X}$ – $p\text{NH}_3$,

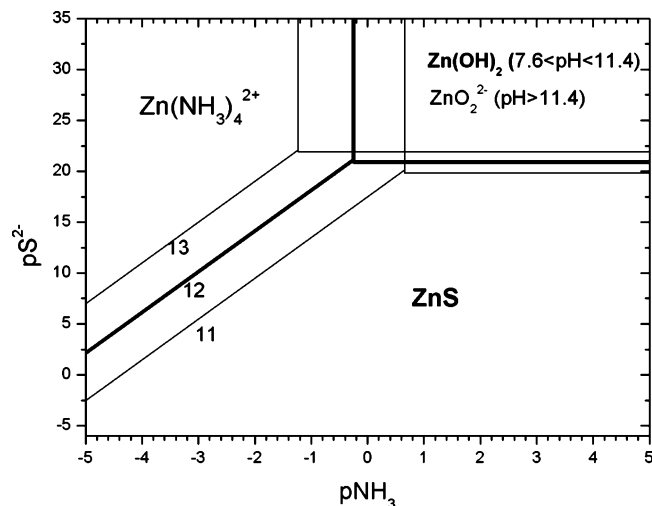


Figure 3. $p\text{S}^{2-}$ – $p\text{NH}_3$ for zinc(II) 10^{-2} M, with lines for three pH values.

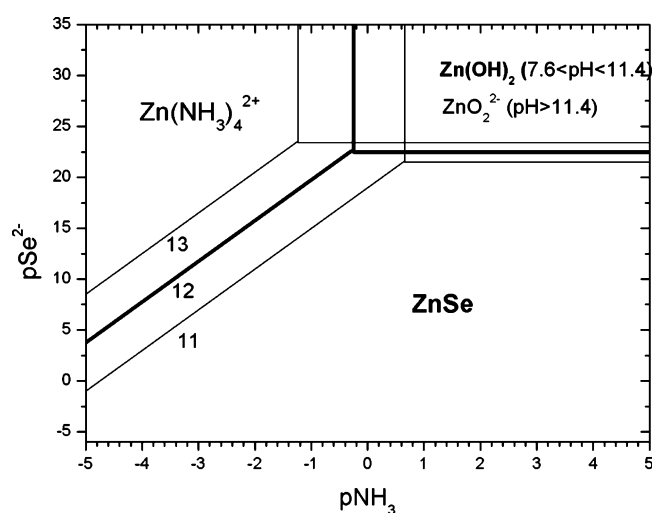


Figure 4. $p\text{Se}^{2-}$ – $p\text{NH}_3$ for zinc(II) 10^{-2} M, with lines for three pH values.

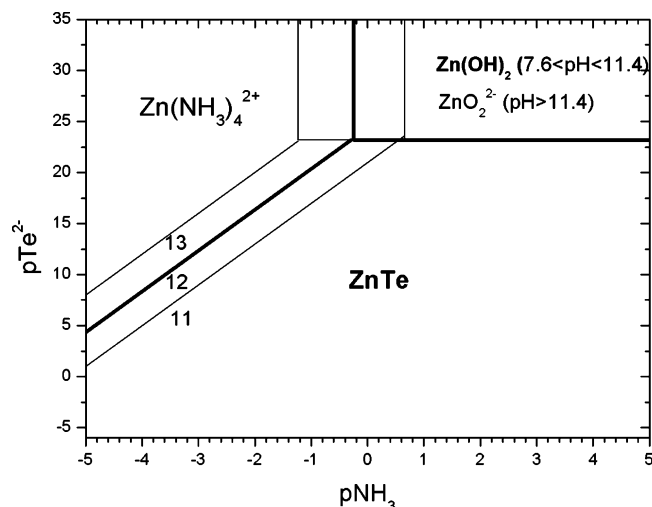


Figure 5. $p\text{Te}^{2-}$ – $p\text{NH}_3$ for zinc(II) 10^{-2} M, with lines for three pH values.

which must be drawn from $p\text{NH}_3$ –pH (Figure 2) and $p\text{X}$ –pH (not shown). Figures 3–5 show the diagrams for the three chalcogenides, including lines at three different pH values. These diagrams will be further commented in the following section.

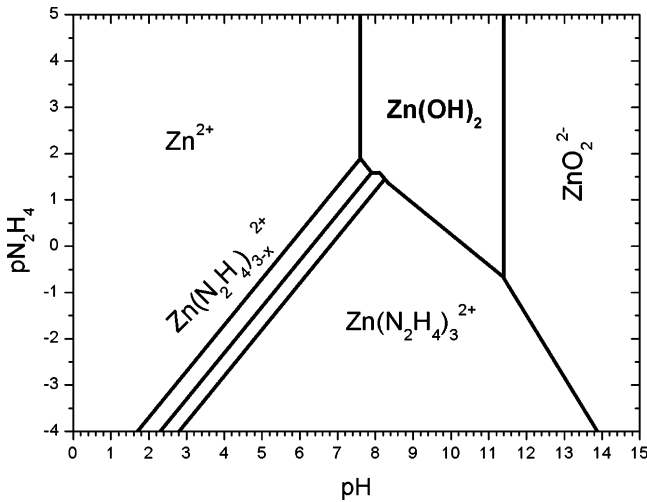


Figure 6. pN_2H_4 -pH diagram of zinc (II) 10^{-2} M.

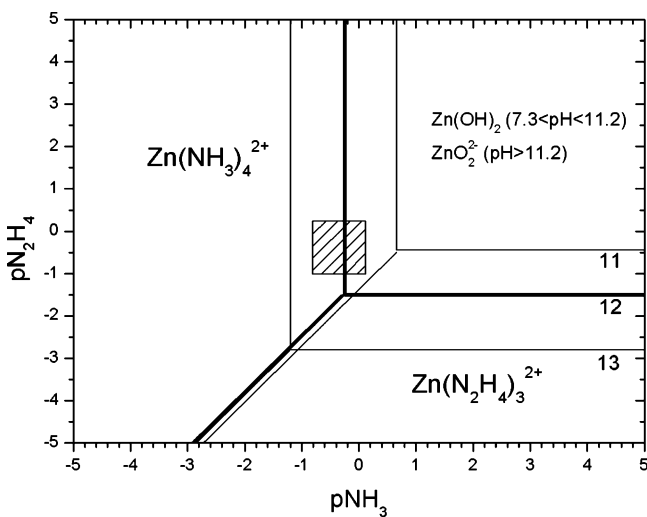


Figure 7. pN_2H_4 - pNH_3 diagram of zinc (II) 10^{-2} M, with lines for three pH values. The dashed area corresponds to the conditions mostly employed for solution deposition of zinc compounds.

One additive of interest for high quality ZnX thin films is hydrazine.^{6,13,14,17,19} Hydrazine is able to form complexes with Zn(II), as shown in the diagram of Figure 6 as a function of pH. It is of interest in our case to make the analysis of zinc complexation in the presence of two complexing agents, ammonia and hydrazine, by means of the pN_2H_4 - pNH_3 diagram of Figure 7. This figure shows that at the pH of interest ($11 < pH < 13$), and under concentrations used in most works (shaded area), the tetra-amino complex ($Zn(NH_3)_4^{2+}$) and the zincate anion (ZnO_2^{2-}) are the predominant species in solution. It means that the reactivity for the formation of zinc compounds should be discussed in terms of these ions. The possibility of formation of ternary amino-hydrazine-zinc complexes is not considered in the diagram because no data are available, although their participation in chemical deposition reactions has been proposed.²⁰ On the other hand, a predominance area for such mixed-ligand species much wider than the line of the $Zn(NH_3)_4^{2+}$ - $Zn(N_2H_4)_3^{2+}$ equilibrium itself is not probable, as it would require unexpected stabilization, for instance by interaction between ammonia and hydrazine ligands.

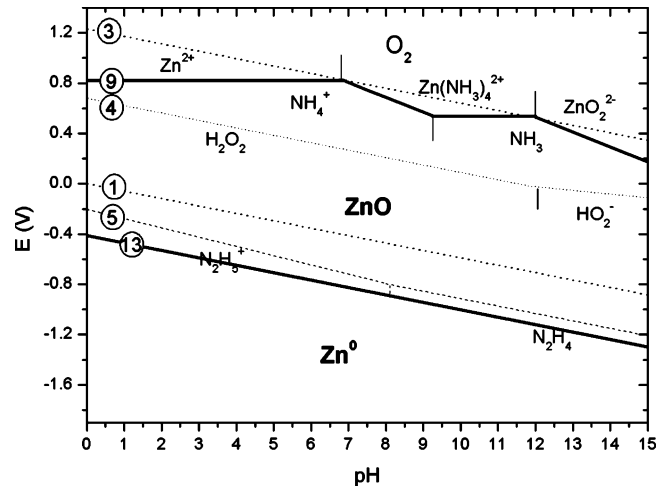


Figure 8. E -pH diagram for zinc 10^{-2} M, NH_3 (1 M), and O_2 (1 atm). Solid compounds are in bold, and main soluble species are indicated in their predominance area. Lines corresponding to water, H_2O_2 , and hydrazine redox equilibria are also included. Numbers indicate the reactions in Table 1.

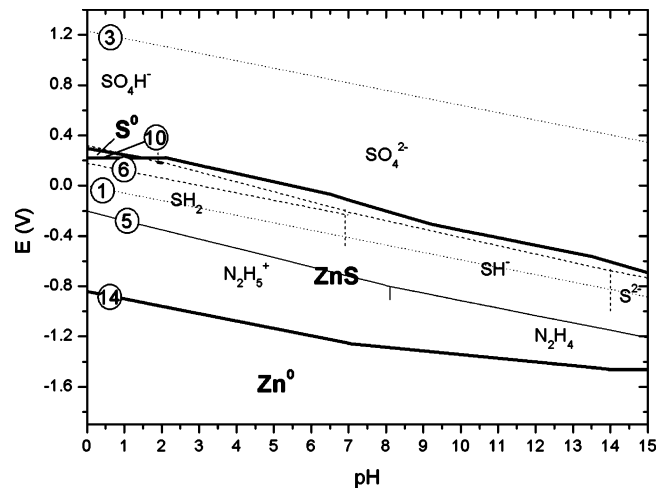


Figure 9. E -pH diagram for zinc 10^{-2} M, sulfur (10^{-2} M), NH_3 (1 M), and O_2 (1 atm). Lines corresponding to water, H_2O_2 , and hydrazine redox equilibria are also included. Numbers indicate the reactions in Table 1.

The electrochemical reactivity of the solution can be analyzed by means of Pourbaix diagrams,²⁵ based on the application of the Nernst equation

$$E = E^\circ + (0.059/n) \log(\prod_i C_i^{\nu_i}) = E^\circ + m - (0.059\nu_H/n) pH \quad (3)$$

where E° is the standard redox potential of the solution, n is the number of electrons in the reaction, ν_H is the stoichiometric number of protons, and the constant (m) includes the logarithmic concentrations (C_i) and stoichiometric numbers (ν_i) of the other soluble species. The construction of the E -pH diagrams requires introducing the pH dependence of the ammonia-zinc species (Figure 2) and of the chalcogenide aqueous equilibria (Table 3). Figures 8-11 show the resulting diagrams for ZnO, ZnS, ZnSe, and ZnTe, respectively. The solid compounds, which will enter the formation of the film, together with some of the soluble species, are indicated inside their respective areas of predominance. The lines of hydrazine and chalcogenide equilibria have also been drawn to discuss their electrochemical reactivity.

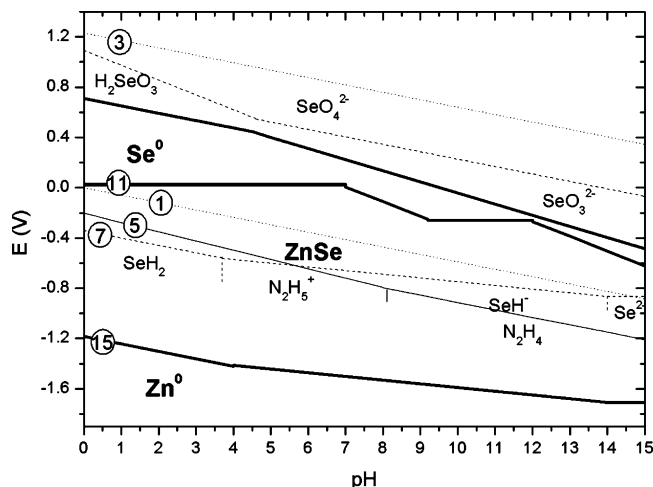


Figure 10. E - pH diagram for zinc 10^{-2} M, selenium (10^{-2} M), NH_3 (1 M), and O_2 (1 atm). Lines corresponding to water, H_2O_2 , and hydrazine redox equilibria are also included. Numbers indicate the reactions in Table I.

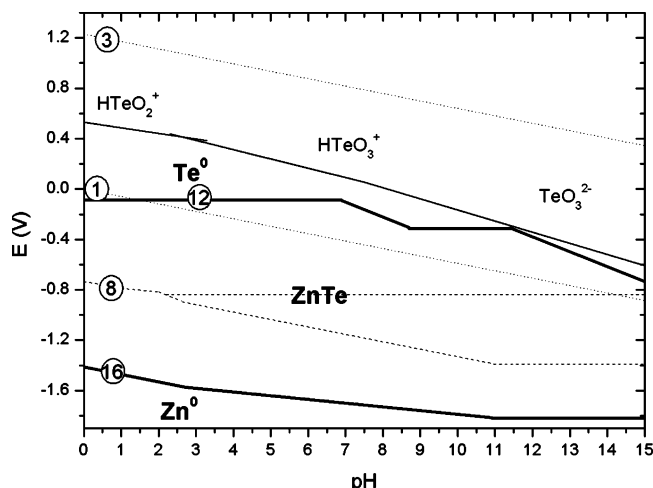
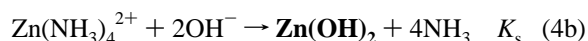


Figure 11. E - pH diagram for zinc 10^{-2} M, tellurium (10^{-2} M), NH_3 (1 M), and O_2 (1 atm). Lines corresponding to water, H_2O_2 , and hydrazine redox equilibria are also included. Numbers indicate the reaction in Table I.

Discussion

Different reactions, chemical and electrochemical, for the formation of zinc compounds are possible in the aqueous solution system described in the previous section. In this section, the different possibilities will be discussed separately (the first through the fourth sections) and later compared in the fifth section.

Chemical Precipitation. Chemical precipitation is possible by reaction of the soluble zinc species, mostly the tetraamino complex ($\text{Zn}(\text{NH}_3)_4^{2+}$) and zincate (ZnO_2^{2-}) (Figure 7), with the chalcogenide anion (X^{2-}) (reaction 4a) or with the hydroxide (reaction 4b)

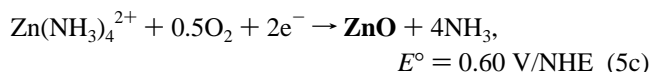
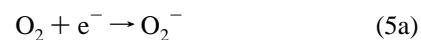


These reactions take place in the bulk of the solution (homogeneous nucleation) or on the substrate (heterogeneous nucleation), giving rise to solid particles that diffuse to, or on, the substrate. As a result, a film grows by a deposition

process, which kinetics obeys to homogeneous chemical solution kinetics²⁷ or heterogeneous chemistry.¹⁰ The high insolubility of chalcogenide favors these reactions from very low concentrations of $[\text{X}^{2-}]$, as shown in the diagrams of Figures 3–5. In these diagrams, the increase in the area of predominance of the compound with pH indicates that the reaction is increasingly favored, the reason being that the species X^{2-} of the chalcogenide is becoming predominant against XH^- . It is also interesting to see that at a more basic pH (>11.4), the predominant zinc species is the zincate anion (ZnO_2^{2-}), which should make it possible to obtain the chalcogenide in the absence of ammonia from a chemical reaction, as has been tried for ZnS .¹⁸ Although chemical precipitation is usually considered the main process for the formation of the films, however, the properties of the films cannot be explained solely from this reaction. Films of ZnS ^{18,19} and ZnSe ^{6,14,17} grown from aqueous solution usually have important proportions of ZnO , and/or hydroxides, as well as oxidized chalcogen atoms. Mixed morphology is also encountered in these films, which show themselves to be compact at short deposition times and more porous at longer times.⁶ On the other hand, kinetics passes through stages with different characteristics.²² These experimental facts must be explained on the basis of different reactions.

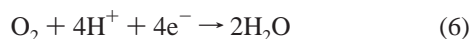
Electrochemical Stability of the Zinc Compounds. The diagrams in Figures 8–11 give a comprehensive view of the electrochemical reactivity of the solution. The location of the predominance area of ZnO and ZnX between the lines of decomposition of water indicates that all of them are stable phases in the whole pH range, except for ZnTe at $\text{pH} < 1.5$, which will oxidize to $\text{Zn}^{2+} + \text{Te}^0$. On the other hand, the predominance area of all solid compounds below the O_2 – H_2O line indicates that none of them are thermodynamically stable phases in oxygenated solution and that the chalcogenides formed, for instance, after reaction 4a, will constitute a metastable phase. This fact is one reason for the high proportion of oxides and oxidized states of the chalcogens usually encountered in chalcogenide thin films. Particularly, the thiourea– $\text{Zn}(\text{II})$ bath gives rise to a mixed ZnO – $\text{Zn}(\text{OH})_2$ – ZnS compound with an important presence of sulfate in the films.^{18,19} The selenourea– $\text{Zn}(\text{II})$ solution results in a ZnSe – ZnO – Se^0 film.^{6,17} For ZnTe , the diagram in Figure 11 predicts the presence of Te^0 in the films.

Electroless–Chemical Formation of ZnO . A consequence of the electrochemical reactivity is the possibility of forming compounds by electroless–chemical reactions (i.e., reactions consisting of an electrochemical step followed by a chemical step). The reduction of oxygen (reaction 5a) and reaction with $\text{Zn}(\text{II})$ (reaction 5b) has been proposed as a route for the formation of ZnO ²²



The overall reaction 5c is thermodynamically very favored in the presence of hydrazine or chalcogenide anions and will

compete with the reduction of water (reactions 6 and 7)



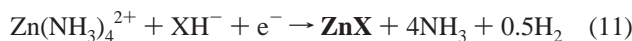
Although reactions 6 and 7 are energetically also favored, reaction 5a competes effectively because it is kinetically most simple, requiring only one electron-transfer per oxygen molecule against four (reaction 6) and two (reaction 7) electrons. The growth of ZnO by electroless-chemical reaction gives rise to compact, adherent, and conforming films.⁶

Electroless-Chemical Deposition of Chalcogenides.

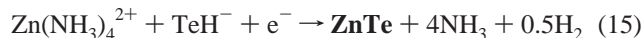
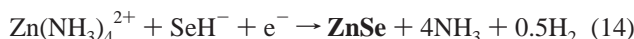
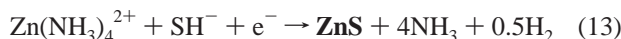
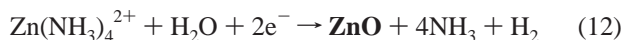
Under oxygen poor conditions in the solution, the reduction of water protons is thermodynamically most favored in the reducing medium imposed by hydrazine and chalcogenide anions (Se^{2-} and Te^{2-} , cf. Figures 8–11). Oxygen poor conditions may be attained by bubbling an inert gas prior to deposition or by increasing the temperature to decrease oxygen solubility.²⁶ In these conditions, the following reaction mechanism for the formation of the chalcogenide may be proposed:



and the whole reaction can be written as



where the XH^- species is preferential at the pH of work. This mechanism is a chemical precipitation induced by proton reduction. Precipitation induced by a reductive process has been proposed for the electrochemical deposition of ZnO.^{28,29} Following the reactions 8–10, the deposition of zinc compounds may be written as



Reactions 8–10 can be considered of electroless-chemical type, where proton reduction is the electrochemical step, followed by chemical precipitation of the compound. Notice that a principal difference between the electroless-chemical deposition of compounds and the electroless deposition of metals is that for the electroless-chemical process, the reducing species may enter the composition of the compound, as for O_2 in reaction 5, or may not, as for H^+ in reactions 12–15. As a result, in the second case, the

Table 4. Characteristics of the Reactions in the Aqueous Zinc Solution for Deposition of Zinc Oxide and Chalcogenides

| no. | 1 | 2 | 3 | 4 | 5 |
|----------------------------|-----------------------------|--------------|--------------|--------------------|--------------------|
| type ^a | C | E-C | E-C | E-C | E-C |
| (semi-) reaction | 4 | 5 | 11 | 5 | 11 |
| reducer | | hydrazine | hydrazine | X^- | X^- |
| oxidant | | O_2 | H^+ | O_2 | H^+ |
| solid product ^b | XZn, Zn(OH) ₂ | ZnO | XZn | ZnO + X^0 | XZn + X^0 |

^a C = chemical and E-C = electroless-chemical. ^b X = S, Se, Te.

compound may be formed without a change in the oxidation state of its elemental components.

Comparison of Different Routes for the Formation of Zinc Oxides and Chalcogenides. The previous sections describe different chemical and electrochemical (electroless-chemical) reactions that may compete in the aqueous zinc ammonia bath for the synthesis of zinc oxide and chalcogenides. The five different reaction possibilities discussed can be classified in two types: (1) chemical precipitation (reaction 4) and (2) electroless-chemical deposition (reactions 5 and 11, including the different combinations with hydrazine or the chalcogenide as the reducer, and with O_2 or H^+ (anoxic conditions) as the reducing species).

The main characteristics and variables are summarized in Table 4. There may be other reaction possibilities, like the oxidation of OH^- , precipitation of the hydroxide, or the formation of metallic zinc, as proposed from a kinetics study,²² that are not considered here because they are thermodynamically little or not favored.

For a comparison of thermodynamic preference among the different reactions in Table 4, Gibbs free energy changes (ΔG) must be considered. A relation analogous to eq 3 may be used for the pH dependence of ΔG

$$\Delta G = \Delta G^\circ + RT \ln(\prod_i C_i^{v_i}) = \Delta G^\circ + m - 5702v_{\text{H}^+}\text{pH} \quad (16)$$

where ΔG° is the standard free energy change, R is the gas constant, T is the absolute temperature, C_i is the concentration of the species, and v_i is the stoichiometric number. Plots of ΔG versus pH are shown in Figure 12 for ZnO and chalcogenide deposition by the different reactions discussed (Table 4). The plots have been calculated for the concentration of species used commonly for Zn compound deposition from aqueous solution. For ZnO and Zn(OH)₂ (Figure 12a), the distinction is made between the chemical precipitation (C) (no. 1) and the electroless-chemical (E-C) deposition induced by hydrazine, in the presence (no. 2) and absence (no. 3) of oxygen. Comparison of Gibbs free energy changes show that ZnO electroless-chemical deposition is energetically always favored in the presence of oxygen, whereas Zn(OH)₂ precipitation is an uphill process at almost any pH, as expected in the ammonia medium used. In the absence of oxygen, ZnO formation is possible only at pH > 3 via reduction of water with hydrazine.

As for chalcogenide deposition, the distinction is made among three possible processes, namely, chemical precipitation (no. 1), electroless-chemical by hydrazine oxidation (no. 3), and electroless-chemical by chalcogen oxidation (nos. 4 and 5 in Table 4). The presence of oxygen will in all cases give rise preferentially to ZnO + X^0 (no. 4). ZnS

(28) Peulon, S.; Lincot, D. *J. Electrochem. Soc.* **1998**, *145*, 864.

(29) Pauporte, T.; Lincot, D. *J. Electroanal. Chem.* **2001**, *517*, 54.

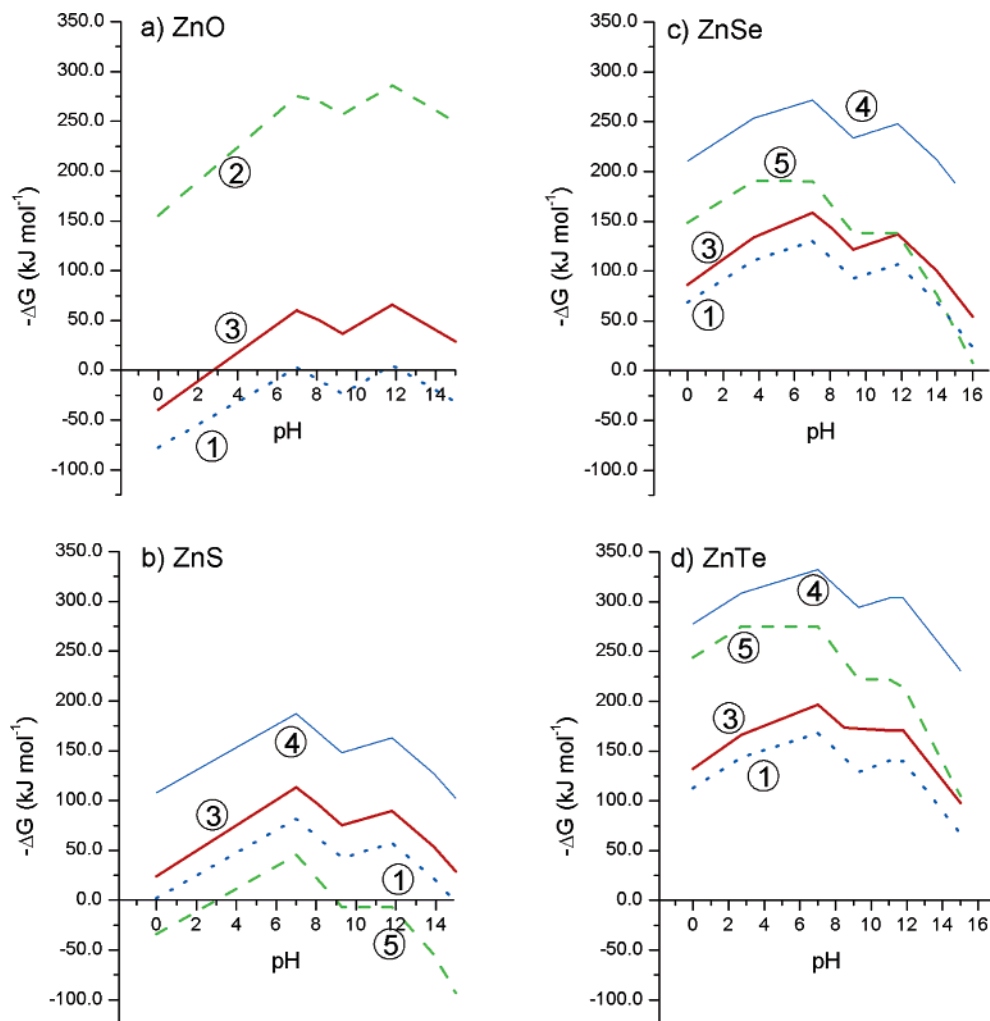


Figure 12. Plots of ΔG vs pH for the aqueous solution synthesis of ZnO (a), ZnS (b), ZnSe (c), and ZnTe (d). Calculated from eq 16 using concentrations zinc(II) 10^{-2} M, X^{2-} 10^{-2} M, NH_3 1 M, N_2H_4 , 1 M, and O_2 1 atm. Numbers correspond to the reaction characteristics in Table 4.

(Figure 12b) will be most favored by E–C via the hydrazine oxidation route at any pH. In the absence of hydrazine, the chemical precipitation will predominate. As for ZnSe (Figure 12c), the preferential route in basic pH will be also the E–C hydrazine oxidation route (no. 3), whereas for $\text{pH} < 12$, it will be the selenide oxidation route (no 5). In this second case, a Se^0 phase will appear together with ZnSe, giving a typical reddish color to the film.⁶ The incorporation of Se^0 can be partially avoided by adding sulfite (SO_3^{2-}) to form the soluble selenosulfite (SeSO_3^{2-}) complex. Compact and transparent ZnSe–ZnO films of interest for a photovoltaic buffer layer may be obtained in aerated solution by parallel E–C hydrazine oxidation, selenide oxidation, and oxygen reduction (nos. 2–4).²² Finally, for ZnTe, the presence of telluride anions in solution would favor the chalcogenide oxidation route, giving the unique possibility of a ZnTe–Te film, as the chemical precipitation is less favored.

Conclusions

The different reaction possibilities for the deposition of zinc chalcogenides and oxide from an aqueous solution have been analyzed by means of thermodynamic diagrams. The

conclusion obtained can be used as a guide for understanding the synthesis of these compounds. It is shown that chemical and electrochemical reactions may contribute to the formation of the compounds. In aerated solutions containing a zinc tetraamino complex, chalcogenide and hydrazine, the most favored reaction is the electroless–chemical formation of ZnO. Here, oxygen reduction gives rise to the growth of ZnO, whereas the zinc chalcogenides, if they appear by chemical precipitation, become metastable compounds. If oxygen is not present, the chalcogenides may be formed by an electroless–chemical reaction consisting of the precipitation of the chalcogenide induced by a reduction of protons. From this reaction type, the formation of ZnS is only possible by hydrazine oxidation; on the other hand, ZnSe may be formed both by hydrazine oxidation at basic pH and/or by selenide oxidation at neutral-acid pH, in this second case producing elemental selenium. Pure ZnTe films cannot be obtained from aqueous solutions but ZnTe–Te or ZnO–Te mixed compositions. In all cases, the pure chemical precipitation reaction is less favored than the electroless–chemical reaction.