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Influence of Selective Nucleation on the One Step Chemical Bath Deposition of CdS/ZnO and CdS/ZnS Composite Films

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We show how the composition and the morphology of composite films deposited by one step chemical bath deposition (CBD) can be controlled by varying kinetic factors, in particular by selective nucleation, as well as varying the rate of growth of specific phases. ZnS/CdS composite films are obtained from a solution containing a mixture of Zn and Cd salts and thiourea under conditions where nucleation of zinc oxide is not favorable, while CdS/ZnO films grow if ZnO nucleation is promoted. In the absence of Cd in the deposition solution, only ZnS forms under all the conditions used by us. The role of Cd in directing the deposition to ZnO is believed to be due to the higher affinity of Cd for S compared to Zn, therefore preventing formation of ZnS in the early stages of deposition and allowing ZnO to nucleate. This demonstrates the importance of interaction between the various components in the solution. Addition of ethanol to the deposition solution, believed to serve as a dehydrating-assisting agent for $Zn(OH)_2$, had a crucial role on the deposition outcome by accelerating formation of ZnO in the bulk of the solution, and leading to more rapid depletion of Zn with respect to Cd.

Introduction

Chemical bath deposition (known also as chemical solution deposition, liquid phase deposition, and sometimes also just chemical deposition, and referred to as CBD in the rest of this manuscript) is an experimentally very simple method of depositing various elements and compounds.[1] Most CBD processes are directed toward the deposition of films of semiconductors, mainly sulfides, selenides, and oxides. In the 1960s, deposition of the Cd chalcogenides, and in particular CdS, was explicitly reported.[2] CdS was for many years probably the most-studied compound deposited by CBD. More recently ZnO has overtaken it in terms of number of studies.

Most films deposited by CBD are binary compounds, although a fairly large range of multicomponent compounds have also been deposited. There are many different "recipes" for CBD, often even for any one material. While CBD used to be more of an art than a science, understanding of the various mechanisms of deposition has advanced to the point where, even if there are still gaps in our understanding of the various processes, and even if "art" still plays a role, we can claim to understand and to predict many CBD processes for deposition of single-phase binary compounds.

Multicomponent systems have been much less studied than binary compounds, and the deposition results are usually less predictable. Some of these multicomponent compounds are true solid solutions; others are mixtures of phases. These multiphase systems were not usually formed deliberately and in fact were unwanted. In some cases (the PbS-CdS system, which thermodynamically is almost immiscible at room temperature, is a common example), formation of separate phases is expected (e.g., ref 3). Metastable solid solutions of $Pb_{1-x}Cd_xS$ have been deposited by CBD up to $x \approx 0.2$; at higher values of x, phase separation occurs and a composite film is obtained.[4,5] In contrast, CdS and ZnS can form solid solutions over the entire range of compositions; yet sometimes solid solutions are formed[6−9] and other times composite films,[10] not to mention cases where insufficient data has been given to judge.[11,12]

More recently, a few papers describing deposition of composite films, emphasizing the composite nature of the films, have appeared in the literature.[13−16] However,

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there is still little fundamental understanding and ability to predict the nature of a CBD composite film.

The choice of solution composition and deposition parameters for deposition of multiphase composite films from a single solution will be determined by three main factors:

(1) The expectation that separate phases, rather than a solid solution, will form (this will be based mainly on thermodynamic factors, which can be predicted).

(2) The ability of each phase separately to be deposited by CBD (and this covers a wide range of materials, more than 50 binary compounds have been deposited by CBD up to now).

(3) Most importantly, the compatibility of the two solutions for the deposition of each constituent separately (i.e., the ability to mix the separate solutions and still get separate phases)

The first two of these criteria are not hard and fast rules, but rather guidelines. For example, for point 1, even if a solid solution is thermodynamically unstable, metastable phases may form as described above for the PbS-CdS system. Regarding point 2, it could be argued that it might be enough to be able to deposit only one component of the composite by CBD, as deposition of the second phase, which would not deposit by itself, could be induced by the first (this is known in precipitation reaction, e.g., coprecipitation of Cr with $Fe(OH)_3$ by adsorption of Cr species on the $Fe(OH)_3$ colloids[17]). This example would also cover point 3, and could be used to illustrate an important principle in CBD of multicomponent systems, whether solid solution or composite: We cannot necessarily assume that a deposition solution containing two comparable components (e.g., two different cations) will behave like a combination of each separately.

We chose to focus on the CdS/ZnO composite system. This composite system of a wide band gap transparent semiconductor with a visible light-absorbing semiconductor is interesting because of its potential photovoltaic properties. This system can also serve as a model for deposition of other composite films. Such a system has been reported where, using a mixture of Cd^{2+} and Zn^{2+}, complexed by ammonia and monoethanolamine (MEA) and containing thiourea (TU), an initial film of CdS was deposited followed by a layer of ZnO nanorods.[13] It is difficult to predict a priori the outcome of such a deposition. While the lower solubility product of CdS implies that it should deposit before ZnS, there are still several options: a solid solution of (Cd,Zn)S; mixed phases of CdS and ZnS; or mixed phases of CdS and ZnO are all reasonably anticipated outcomes. The possibility of ZnO (or $Zn(OH)_2$) deposition, even though TU is present, is known for the Zn−O−S system in CBD.[18−20]

There are a number of different possible mechanisms for deposition of the relevant materials. For ZnO, the generally accepted mechanism is through dehydration of Zn-hydroxy species, which occur in the deposition solution, to form ZnO.[21,22] The deposition is normally carried out at relatively high temperatures of 60−90 °C, which facilitate dissociation of the Zn complexes in the solution as well as dehydration to ZnO. There are a number of possible mechanisms involved in the deposition of metal sulfides, most commonly deposited from alkaline solutions using TU as a source of S. One, the ion-by-ion mechanism involves direct reaction between Cd^{2+} and S^{2-} ions (the latter formed from hydrolysis of TU). The second, the cluster mechanism, is a reaction of S^{2-} with $Cd(OH)_2$ colloids in the solution.[23] Another possible route, which does not require free S^{2-} ion, is decomposition of a Cd-thiourea complex, either as a soluble species or as thiourea bonded to a solid $Cd(OH)_2$ particle (complex decomposition).[24]

In the present study, we combine our previous experience of CBD CdS, ZnS, and ZnO and show how codeposition from a multicomponent solution can be directed along different pathways giving films possessing different compositions, phase distributions, and morphologies. We show that this can be done by judicious selection of the deposition conditions and, very importantly, by promoting selective nucleation of the ZnO phase. We also show that, although thermodynamic considerations such as solubility products are important, kinetic considerations can sometimes determine not just the morphology or phase distribution of a film, but even its basic chemical nature.

Experimental Section

Films were deposited on soda-lime glass microscope slides and/or Pilkington TEC 7 fluorine-doped tin oxide (FTO) coated conductive glass.

All substrates were cleaned in an ultrasonic bath for 20 min by Alconox detergent solution preheated to 70−80 °C. Substrates were then extensively rinsed in Millipore deionized water (DW) followed by sonication for 5−10 min in DW in an ultrasonic bath and finally rinsed again to remove any remaining traces of the detergent.

Film deposition was performed on both unactivated substrates and on substrates activated by four different methods:

Preactivation of the substrate by $KMnO_4$ solution.[25]

In situ activation of the substrate by using monoethanolamine (MEA; one of the complexes) containing Fe.[26]

A combination of both the above activation methods.

Activation by nanocrystalline ZnO (used only in one control experiment).

Substrate Activation. *$KMnO_4$ Preactivation.* The substrates were placed in glass vials filled with 0.5 mM fresh $KMnO_4$

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Table 1. Deposition Parameters Used in the Present Study

	main screening set of experiments	influence of Cd^{2+} on the deposition of ZnO in the presence of TU	
substrate activation	**yes/no**	yes	no
Zn^{2+}	**50/100 mM**	0.1	0.1
Cd^{2+}	**25/50 mM**	**0–2.5 mM**	**0–2.5 mMM**
ethanol	**no/25% v/v**	no	no
NH_3	**0.3–0.6 M**	0.4 M	0.4 M
total amount of MEA	1.7 M (10% v/v)	1.7 M (10% v/v)	1.7 M (10% v/v)
MEA:Fe:MEA ratio	**0–1.5**	0	0.4
TU	**25–100 mM**	**50/100 mM**	**50/100 mM**
deposition temperature	**75/90 °C**	**75/90 °C**	**75/90 °C**
deposition time	**15/45/120 min.**	45 min	45 min

solution and 50 μL of *n*-butanol per 20 mL of the permanganate solution were added. The vials were closed and placed in a water bath at 85−90 °C for 20 min. Permanganate-treated substrates were extensively rinsed in DW. More details about the activation technique and the importance of adequate rinsing can be found in our previous work.[25]

In Situ Activation by Use of MEA Containing Fe (*Designated As MEA:Fe; Pure MEA Will Be Designated as MEA*). Fe^{3+} (or Fe^{2+}) iron salt (ferric chloride or ferrous ammonium sulfate) is first dissolved in 0.5 mL of water and then immediately mixed with 49.5 mL of MEA to give MEA containing 100 ppm of Fe. The resulting solution is filtered through a 0.22 μ PVDF syringe filter 2 weeks after its preparation. The concentration of Fe in the filtered solution was found by ICP to be ~50 ppm. More details of the Fe activation of the solution and of ZnO deposition using MEA:Fe have been described by us previously.[26]

Nanocrystalline ZnO Activation. Predeposition of nanocrystalline ZnO is a commonly used activation (seeding) treatment for ZnO deposition. It was used on only one occasion in this study to show the generality of the conclusions. Nanocrystalline ZnO film was prepared using a sol−gel method described by Li et al.[27]

Film Deposition. Deposition solutions were prepared using the following aqueous stock solutions: 1.0 M $ZnNO_3$ (for some experiments, $ZnSO_4$, or $ZnCl_2$ were used and gave qualitatively similar results), 0.5 M $CdCl_2$, 4.0 M ammonium hydroxide, 50% (by volume) aqueous MEA or MEA:Fe, 1.0 M thiourea (TU). The final deposition solution was prepared from the stock solutions in 20 mL borosilicate glass vials by sequential addition to water of ethanol (in cases where it was used), zinc salt, cadmium salt, ammonia, and MEA (or MEA:Fe) and TU (TU was added just after the substrate was placed in the solution). The substrate was placed slightly inclined from vertical to prevent particles which form in the solution from settling on the downward-facing side of the substrate, the side chosen for characterization. The amount of water was chosen so that the total volume of each solution was 10 mL. Immediately after the solution preparation, the reaction vial was closed and placed in a water bath.

Table 1 summarizes different deposition parameters that were used. The influence of each of the underlined parameters was examined independently and also in combination with varying other underlined parameters.

All results shown below are for films grown at 90 °C. Experiments were also carried out at 75 °C: while there were some differences in ZnO morphology and the results were somewhat less reproducible than those at 90 °C, the overall picture explained later did not change. The pH was not deliberately adjusted; however, the pH of all solutions was between 10.8 and 11.0.

The most reproducible results were obtained using "standard" deposition conditions. For depositions on $KMnO_4$ activated substrates, we designate standard deposition as deposition from a solution containing 100 mM $ZnNO_3$, 25 mM $CdCl_2$, 0.4 M NH_3, 1.7 M MEA, 50 mM TU and 25% v/v of ethanol at 90 °C for 45 min. (We ignore any small volume change due to mixing of different solution components in calculation of the final concentrations) For in situ activation deposition, the standard solution composition contains a MEA:Fe:MEA ratio of 0.4 which corresponds to 1.5 ppm of Fe in the deposition solution, 100 mM TU, and does not contain ethanol. We define three different TU concentrations: high (100 mM); medium (50 mM); and low (25 mM).

Deposit Characterization. Films deposited on the bottom side of the substrates were first visually inspected to monitor coating uniformity on a macro scale. (Deposits from the top side were removed using dilute HCl (ca. 5% conc. HCl in water). The films were examined with a high resolution "Ultra 55" FEG Zeiss scanning electron microscope, a Rigaku sealed tube generator-based ULTIMA III X-ray diffractometer, and a Jasco V570 UV−visible spectrophotometer equipped with an integrating sphere. All presented optical spectra were corrected for reflection and normalized. Collected powders for X-ray diffraction (XRD) were rinsed three times with DI water, each rinse followed by centrifugation and decantation.

Results

As it is very relevant to the present study, we briefly recap our previous work on surface activation of ZnO deposition. In the absence of some nucleation agent (whether in situ as in the case of Mn or Fe ions added to the deposition solution,[26] or by a pretreatment (seeding) of the substrate[25]), little or no ZnO deposited on glass substrates from alkaline ethanolamine-based deposition solutions. In the presence of one of the above nucleation strategies; however, uniform ZnO films having a nanorod morphology were obtained (Supporting Information, Figure S1). The activation allows facile nucleation due to adsorption of Zn species on the hydrated Mn or Fe oxide nuclei. The areal density of the ZnO crystals and the film morphology (ZnO crystal size, aspect ratio and directionality/texture) could be tailored by varying activation conditions, the complexant:Zn concentration ratio, choice of the anion of the zinc salt,[25] and by small variations in pH (higher pH of the deposition solution results in films with narrower ZnO crystals).

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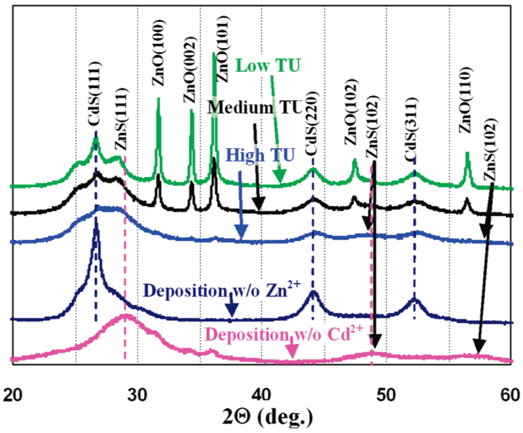

Figure 1. XRD pattern of powders precipitated from non-activated deposition. (Note for CdS and ZnS, we assume cubic to be a dominant phase, but the shoulders around the CdS (111) peak indicate that considerable amounts of hexagonal CdS phase are formed.).

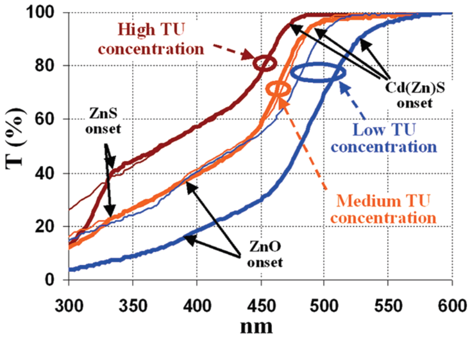

Figure 2. UV–visible spectrum of the films deposited without activation. Thin and thick lines represent 15 and 90 min depositions, respectively.

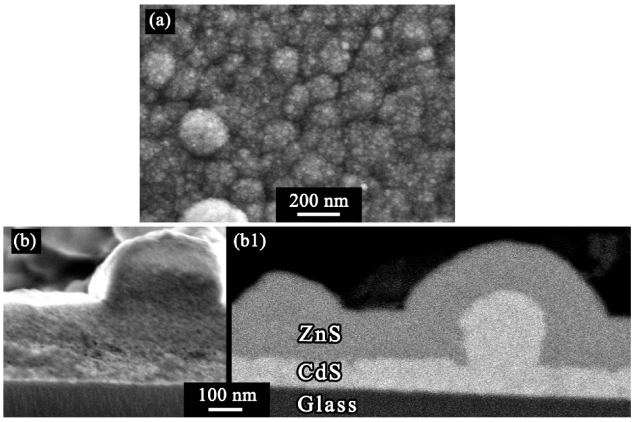

Figure 3. SEM images of the composite film deposited for 90 min without activation. (a) Secondary electron plan view. (b) Secondary electron cross-section view, (b1) backscattered electron cross-section view.

These same activation techniques that dictate whether or not ZnO is deposited are also found to dictate the nature of composite deposition involving Zn^{2+} ions. The basic system we use contains Zn^{2+}, Cd^{2+}, thiourea (TU) (as a sulfur source), and monoethanolamine (MEA) and ammonia as complexing agents. We first describe the deposition carried out in the absence of any seeding (nucleation) procedure.

Composite Deposition in the Absence of Substrate Seeding. When deposition is carried out on non-treated substrates and in the absence of any seeding “impurity”, ZnS/CdS bilayer films are always formed from solutions containing Cd and Zn ions and TU.

XRD of precipitates formed from the depositions are shown in Figure 1 (the films showed only very weak peaks). At high concentrations of TU, the XRD pattern suggests a mixture of CdS and ZnS (the high angle peaks show both ZnS and CdS, although the high angle, high concentration TU CdS peaks are slightly shifted to larger angles, suggesting ≈5% Zn in the CdS). The low angle broad peak is more difficult to interpret since, taken by itself, it could represent either a mixture of (at least partially) hexagonal CdS and cubic ZnS or a solid solution of (Cd,Zn)S. As the TU concentration is reduced, the presence of essentially pure-phase CdS becomes apparent, together with a weak ZnS signal. Also, ZnO appears, and its concentration increases as the TU concentration becomes lower. We note that only a ZnS film is formed when there is no source of Cd in the solution, and only CdS when there is no source of Zn.

Optical spectra of the films can be used to distinguish between ZnS and ZnO, as long as the films are not too thick (so that there is still considerable transmission in the UV region). Figure 2 shows that at high TU concentration, no ZnO absorption is seen but only that of ZnS, while at low TU concentration, there is a small, but clear absorption onset due to ZnO (medium TU concentration shows a clear ZnS onset but no clear ZnO absorption). Also, from a comparison of the short and longer time depositions (particularly evident in the high TU concentration examples), it can be seen that CdS deposits first, followed by the ZnS. The CdS onsets occur over an almost 50 nm range (estimated equivalent bandgap from 2.36–2.61 eV). The most probable explanations for these blue shifts (the “normal” bandgap of CdS is ca. 2.4 eV) are either size quantization and/or formation of a (Cd,Zn)S solid solution. From the width of the XRD peaks, little or no size quantization of the CdS is expected. At the same time, as previously noted, the high angle XRD peaks show little sign of solid solution formation, except for the high concentration TU sample with ≈5% Zn (which would increase the bandgap by ca. 30 meV[28]). The shift in onset of the “CdS” absorption seems to be related more to the film thickness than to the TU concentration (compare the low TU concentration thin and thick spectra).

Scanning electron microscopy (SEM) imaging of one of these films is shown in Figure 3. Cross-sectional imaging in the backscattered mode, in particular (Figure 3b1), provides clear structural information on the composite structure. It confirms, as inferred from the optical spectra, that CdS deposits initially and that the ZnS deposits on top of the initial CdS layer. SEM also shows that the ZnO seen in the XRD and optical spectra of the low and medium TU concentration deposits (precipitates) is invariably in the form of spurious precipitates attached to the films and not as an ordered film (Supporting Information, Figure S2).

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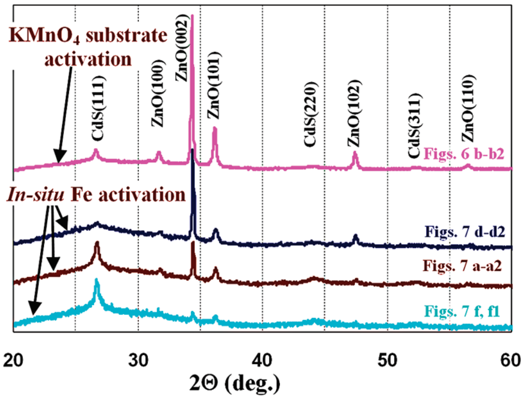


Figure 4. XRD patterns of ZnO/CdS composite films. (The number of the corresponding SEM images are given above each curve.).

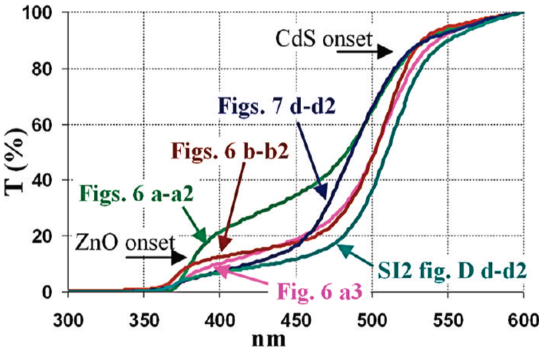


Figure 5. UV−visible spectra of ZnO/CdS composite films. (The number of the corresponding SEM images are given beside each curve.).

CBD ZnS films often contain zinc hydroxy species.[18,19,29−31] However, we do not address this issue here.

Composite Deposition with Substrate Seeding. The nature of the film is very different if the substrate is seeded, either in situ (by adding Fe to the MEA with a final deposition solution Fe content of down to 0.75 ppm) or by permanganate substrate activation (see Experimental Section for details). In this case, a CdS/ZnO composite, rather than CdS/ZnS, is obtained for mixed Cd−Zn deposition when the concentration of NH_3 is less than 0.5 M.[32] Above this concentration, ZnO does not form (under these conditions, CdS followed by ZnS is obtained as in the case of no substrate activation). The presence of both CdS and ZnO can be seen by both XRD and UV−vis spectra (Figures 4, 5) although the morphology and dispersion of the two components can be varied considerably as shown below (Figures 6, 7, and Supporting Information, Figures S3, S4).

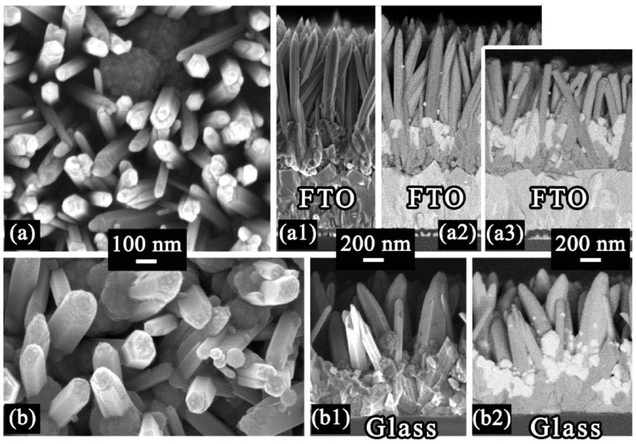
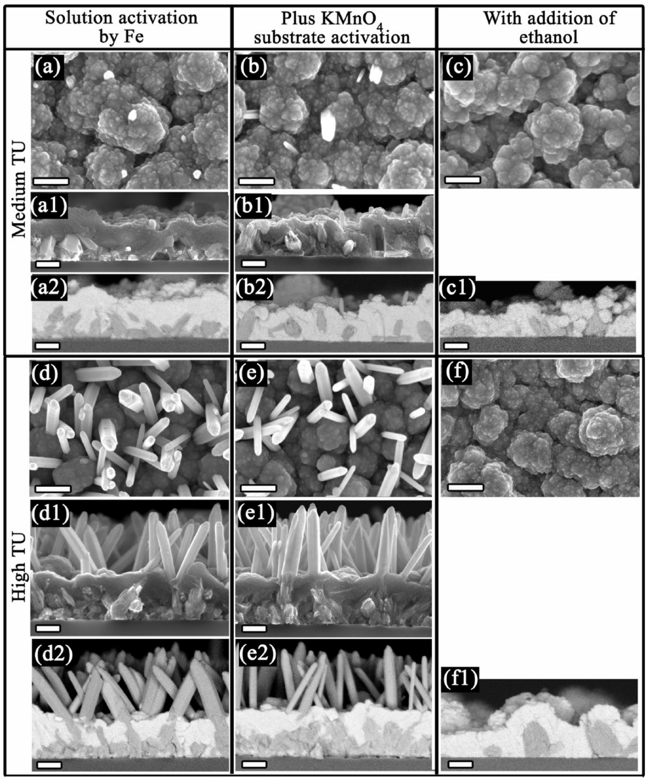


Figure 6. SEM images of composite films deposited from a solution containing MEA and ethanol on $KMnO_4$-activated substrates. (a) Plan view, (a1) cross-section view, (a2,3) backscattered cross-section view of films deposited on FTO. (b) Plan view, (b1) cross-section view, (b2) backscattered cross-section view of film deposited on glass.



All scale bars represent 200 nm

Figure 7. Plan, cross-section, and backscattered cross-section SEM images of composite films deposited on non-activated and on $KMnO_4$-activated glass substrates using MEA:Fe (in situ solution activation by Fe) with and w/o addition of ethanol; (medium and high TU concentrations).

$KMnO_4$-Activated Substrate. On $KMnO_4$-activated substrates, reproducible composite film formation is only found if ethanol is added to the deposition solution and for medium TU concentration. Ethanol is known to promote ZnO formation from $Zn(OH)_2$ by dehydration;[33] in our studies here, we find that it accelerates the formation of

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(32) Roughly above this concentration of ammonia, ZnO does not form (the limiting concentration will, of course, depend also on the Zn and Cd concentrations). Higher ammonia concentration prevents formation of the relatively soluble (compared to ZnS) $Zn(OH)_2$ or ZnO. Higher concentrations of ammonia also increases pH that in turn also promotes $Zn(OH)_2$ dissolution and TU decomposition to give a reactive sulphide.

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ZnO, including precipitation in the bulk of the solution (in all the depositions described here, there is considerable bulk precipitation along with film deposition). Some variation in film morphology, thickness, and phase distribution does occur from deposition to deposition. For example, the films shown in Figure 6a2 and a3 were deposited under nominally identical conditions. Figure 6 shows examples of composite depositions on both glass and FTO. While there are differences in the ZnO rod diameter (the rod diameter on glass is considerably broader than on FTO), the general composite picture is similar on both substrates, with ZnO (darker in the backscattered images) growing from the substrate and CdS (lighter in the backscattered images) depositing in between the growing ZnO. The ZnO continues to grow after the CdS growth terminates (presumably when most of the Cd has been removed from solution).

As we noted, in the absence of ethanol, deposition on $KMnO_4$-activated substrates is not reproducible and usually non-uniform. Supporting Information, Figure S5 shows examples of such depositions. Either dense and thick ZnO films with very little CdS inclusions (Supporting Information, Figures S5a,b) or films with mixed morphology possessing composite ZnO/CdS regions together with pure CdS regions (Supporting Information, Figures S5b1,c) were formed. In addition, in contrast to deposition of ZnO by itself, where the $KMnO_4$-activated substrate is a very efficient nucleation enhancer, in the presence of a high concentration of TU, this no longer is the case.

In Situ Activation by MEA:Fe. In situ activation of glass by MEA:Fe is shown in Figure 7, left column, for two different TU concentrations. For medium TU, mainly ZnO (some CdS is also seen) grows on the glass followed by CdS deposition as in the $KMnO_4$–activated substrate. However, in this case, the CdS blocks further growth of ZnO nanorods, except for the appearance of occasional small protrusions of ZnO above the CdS (white areas in the plan view; Figure 7a). For high TU concentration, while the initial growth is similar, ZnO nanorod growth above the CdS/ZnO underlayer is much more extensive, although still not dense in absolute terms (Figure 7d). This further growth of ZnO contains no CdS and must occur when there is too little CdS and/or TU left in solution to deposit CdS. This TU dependence could be explained by faster deposition of CdS, leaving more Zn^{2+} in solution for further ZnO growth. More detailed discussion of the composite deposition will be covered in the General Discussion section.

Addition of ethanol, with its relatively rapid removal of ZnO by bulk precipitation, results in short and sparse ZnO growth, allowing coverage of the ZnO by CdS (Figures 7c1,f1), which itself can prevent further ZnO growth (even if sufficient Zn remained), as noted above.

The results for MEA:Fe activation using FTO substrates instead of glass were somewhat different in detail. ZnO grew preferentially in both medium and high TU solutions (rather than just high TU as for glass substrates) and there was less CdS deposition overall compared to glass substrates (see Supporting Information, Figures S3 and S4c). Also, addition of ethanol depressed ZnO crystal length only for high TU, but not so much for medium TU conditions. These differences all emphasize the crucial role of nucleation in determining the nature of composite deposition, consistent with our knowledge that ZnO alone nucleates better on FTO (some deposit without activation and denser films with activation).

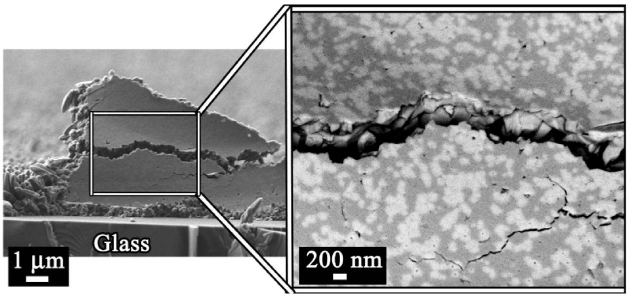


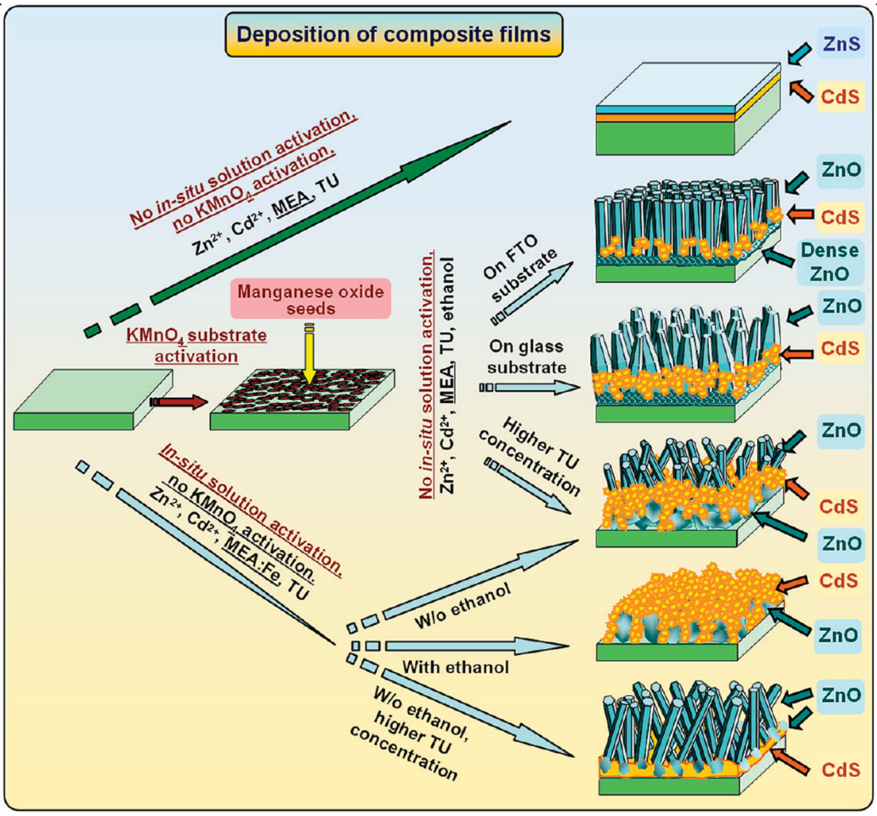
Figure 8. Backscattered SEM image (right figure) showing the composite nature) of the bottom side of a partially detached film (shown in the left figure) deposited on a glass substrate using MEA:Fe activation (High TU concentration, w/o ethanol).

In this general system, we fortuitously were able to obtain a backscattered plan image of the bottom of a film that has become detached from the substrate (Figure 8). This image clearly shows that, under the conditions of this deposition, both ZnO dark regions) and CdS (light regions) formed at the start of deposition. This can be compared with Figure 7d2, where CdS and ZnO are also observed growing from the glass substrate, or Supporting Information, Figure S3a1, where the same is seen on a FTO substrate. However Figure 8 shows this over a relatively large area in the substrate (x-y) plane rather than the x-z displays afforded by the cross sections.

MEA:Fe + $KMnO_4$ Activation. Activation by both MEA:Fe + $KMnO_4$ on glass led to lower reproducibility and also less homogeneous films (seen visually) compared to MEA:Fe activation only. However, in spite of this, there were some interesting trends for this double activation (Figure 7, middle column). As for MEA:Fe activation alone, ZnO nanorod growth through the CdS was limited using medium, rather than high TU conditions. However, the distribution of CdS around the ZnO was better for the double activation (compare Figure 7b2 with 7a2). This occurs because of the more dispersed growth of ZnO in the double activated case, allowing CdS to grow both on the substrate and around the ZnO. Not only is double activation not better for ZnO nucleation than either activation method separately, but the $KMnO_4$ activation actually reduces the efficiency of the MEA:Fe activation. Since the latter is due to adsorption of hydrated Fe oxide colloids on the substrate,[26] it seems that the hydrated Mn oxide present on the substrate reduces this adsorption. For the high TU solutions, there is little difference in the films obtained with double activation and MEA:Fe only.

Nanocrystalline ZnO Substrate Activation. To show that the above results are valid for other seeding procedures and not just for the specific seeding methods used

Scheme 1. Schematic Summary of the Main Results



by us above, we carried out deposition on nanocrystalline ZnO which is widely used as a seeding layer for ZnO deposition.[34-37] The SEM image in Supporting Information, Figure S6 shows that also with this seeding method, a ZnO/CdS composite is obtained.

Role of Cd in Determining the Deposition. It is important to note that no ZnO was formed from TU-containing solutions that did not contain some Cd^{2+}, even when seeding was used. One mM of Cd^{2+} was however sufficient to promote formation of ZnO instead of ZnS (with no detectable co-deposition of CdS at that concentration). We assume that the Cd^{2+} preferentially reacts with sulfide gradually formed from the TU decomposition because of the lower K_{sp} of CdS, thus preventing formation of ZnS and allowing nucleation of ZnO on Fe−O or Mn−O or predeposited ZnO nucleation centers. The role of Cd is summarized in the scheme in Supporting Information, Figure S7.

Finally, we note that very preliminary experiments on the photoelectrochemical activity using the as-deposited ZnO/CdS composite films in polysulfide electrolyte showed a promising photoelectrochemical response of up to 350 mV open circuit voltage and 0.25 mA/cm^2 short circuit current under approximately 1 sun illumination.

General Discussion

We first sum up the main observations from this study (shown also in schematic form in Scheme 1 and Supporting Information, Figure S7).

On non-activated glass and FTO substrates, deposition from an alkaline, complexed solutions of Cd^{2+}, Zn^{2+}, and TU always resulted in a bilayer film of ZnS on CdS (or in some cases, ZnS on CdS containing several percent ZnS as a solid solution). This is in accord with a number of studies that claim slower formation of ZnS compared with CdS from alkaline TU solutions.[18,19] A little ZnO may also occur in the film under some circumstances, but this is probably due to spurious attachment of ZnO or Zn(OH)$_2$ clusters from the solution.

Under the same conditions, but on activated substrates, a composite of ZnO and CdS is obtained. The details of the distribution between the two components vary depending on other parameters, in particular the substrate used, the mode of substrate activation, TU concentration, and presence of ethanol. The most common and reproducible form we have encountered is predominantly relatively dense ZnO (with varying amounts of CdS), followed by a mixture of ZnO and CdS. This may be followed by further growth of ZnO nanorods from the underlying ZnO surfaces. If CdS completely covers the ZnO, then further growth of ZnO does not occur.

Solutions containing Zn^{2+} + TU without any Cd (activated or non-activated substrates) give ZnS films. Addition of Cd^{2+} (at least 1 mM) to these solutions on

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activated substrates changes the deposition from ZnS to ZnO (together with varying amounts of CdS).

There are several interconnected issues that need to be considered to explain our results:

(a) ZnO deposition on many substrates (including glass and FTO conducting glass) requires activation (either preactivation or in situ activation) in order for reproducible ZnO nucleation and deposition to occur (noted at the beginning of the Results section). This is in contrast to many other compounds, including CdS and ZnS, that are much less dependent on the nature of the substrate

(b) Timing and distribution of nucleation of ZnO and CdS on the substrate.

(c) Relative growth rate (and as a result depletion of reagents in solution) of the two components, both on the substrate (film growth) and in the solution (precipitation).

(d) Ability of each component to nucleate (and grow) on the other component. On the basis of experiments not described here, neither CdS nor ZnS films serve as nucleation-promoting substrates for ZnO formation. Also, while CBD CdS can grow on ZnO, it does so only in a cluster mode (using an alkaline TU deposition bath), as observed by us and by others.[38,39]

On non-activated substrates, ZnO does not nucleate readily. Therefore either CdS or ZnS, which are not so susceptible to the nature of the substrate for nucleation, will nucleate and grow. Since thermodynamically, CdS can deposit more readily than ZnS (e.g., lower K_{sp} of CdS, stronger complexation of Zn by ammonia), we obtain an initial layer of CdS followed by ZnS when the Cd concentration becomes sufficiently low to allow its growth. The fact that we obtain two separate phases rather than a solid solution of (Cd,Zn)S (we do find small percentages of Zn as solid solution in the CdS under some conditions), is not unusual: CBD of ternary compounds, even ones as similar as Cd and Zn, often form separate phases rather than solid solutions. In addition to thermodynamic considerations, there are several other possible explanations for whether solid solution or separate phases form, for example, deposition mechanism (for ion-by-ion deposition, CdS is thermodynamically expected to deposit first, while for a cluster mechanism, the outcome will depend on the composition of the hydroxide clusters) or the existence of Zn(OH)S phases.

On activated substrates, where ZnO nucleates readily, it competes with CdS nucleation and can even dominate the initial deposition. The ratio of ZnO and CdS in this nucleation will depend both on substrate activation and on deposition parameters. If there is a high density of activation centers on the substrate, favoring ZnO growth, we expect mainly ZnO to nucleate and once ZnO nucleates on the substrate, it will continue to grow. (A higher density of more finely dispersed activation centers is also expected to result in narrower nanorods since there will be more ZnO nuclei early in the deposition competing with a fixed concentration of Zn. This is seen in Figure 6, where the Mn−O nuclei are more finely dispersed on FTO compared to glass.[25]) However, a high density of nucleation centers by itself does not guarantee a dense layer of ZnO: Depending on the deposition parameters (e.g., higher TU concentration will increase CdS growth rate or addition of ethanol increases ZnO growth rate), the ratio of ZnO to CdS will vary in the initial growth (e.g., mainly ZnO Figures 6a3,b2, 7d2,e2 or comparable amounts of both ZnO and CdS Figures 7b2, Supporting Information, Figure S3a1). If precipitation of ZnO in solution is very extensive early in the deposition (e.g., addition of ethanol or Fe solution species, both of which induce ZnO precipitation), this causes strong depletion of Zn^{2+}, reducing the ZnO growth rate in the film and thus increasing the relative amount of CdS (Figure 7c1,f1). We note that this depletion of Zn^{2+} is not necessarily the same as reducing the Zn concentration in the initial solution, since a lower Zn concentration may affect not only growth, but also nucleation.

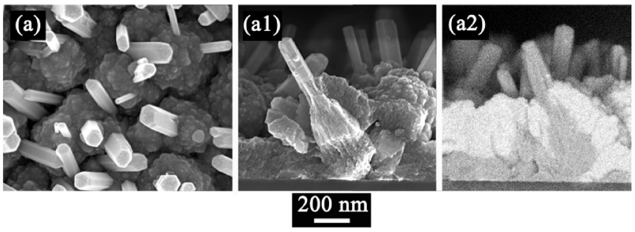

Figure 9. Plan, cross-section, and backscattered cross-section SEM images of a composite film deposited on a $KMnO_4$-activated glass substrate using a solution containing MEA, ethanol, and high TU concentration.

After successful nucleation, growth of ZnO is fastest early in the deposition, as it does not depend, like CdS, on generation of reactive species (resulting in an induction time for start of CdS growth). Thus, at some stage in the growth, the CdS:ZnO ratio will increase (due possibly to both increase in CdS formation rate and decrease in ZnO growth). This increased CdS growth will block, to a greater or lesser extent, the continuing ZnO growth (ZnO cannot renucleate on CdS). The fact that CdS does not grow conformally on ZnO under the conditions used by us, but rather as clusters (as noted earlier), allows ZnO to penetrate through growing CdS (Figures 7d-d1,e-e1). This is also seen particularly clearly in Figure 9, where ZnO starts to grow as thick rods (when the Zn^{2+} concentration is high); these rods are partially blocked with CdS later in the growth, and finally ZnO rods continue to grow, but with reduced diameter (since the concentration of Zn^{2+} is now much lower and it is well-established that ZnO nanorod diameter is roughly proportional to the Zn^{2+}concentration[40]). If at this growth stage, mainly because of extensive precipitation, there is essentially no Zn^{2+} left in solution, no further growth of ZnO will occur

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(Figures 7a,b). If there is less precipitation of ZnO in the solution (e.g., substrate activation by $KMnO_4$ (Figure 6)), ZnO will continue to grow after all the solution Cd^{2+} has been depleted and/or the growing CdS clusters become too large to contribute to CdS film formation (smaller clusters tend to adhere better than do large ones). On the basis of the solution composition, we assume the CdS deposition occurs by a cluster mechanism rather than an ion-by-ion mechanism.[23] Thus the CdS grows by adsorption of $Cd(OH)_2$, partially sulfided $Cd(OH)_2$, or CdS colloids from the solution onto the growing film.

The basic deposition process used in this work was taken from ref 13, where a composite ZnO-on-CdS film was obtained. We had repeated this deposition as a first step in studying CBD composite films, and found that we obtained ZnO/CdS films using MEA that was (fortuitously) contaminated with Fe, but always ZnS/CdS films using pure MEA. This led us to study the effect of Fe[26] and (because of expected similarities) Mn[25] on ZnO deposition and eventually back to the study described in this paper. The ZnO/CdS films of ref 13 were obtained on non-activated glass substrates, which raises the question "what was the difference between the two studies?". The presence of a nucleation-promoting impurity in the deposition bath of ref 13 is one possible explanation for this apparent discrepancy.

In spite of the extensive investigation of the effect of deposition parameters on the films, there are still other parameters that we have not studied for this deposition and which would probably provide even more insight into the deposition mechanism(s). Examples are as follows: a wide variation of the Zn (and Zn:Cd ratio) concentration (to be compared with rapid removal of Zn by homogeneous precipitation, thus separating nucleation effects from growth effects), and the effect of pH, which can have many different effects on the deposition.

Conclusions

We can conclude that, for CBD of composites, understanding the factors that influence the deposition of each phase separately, while important, is not necessarily sufficient. Both the start of nucleation of each phase, the relative growth rates of each, and interactions between the different species in solution are additional important factors in determining the nature of the films. In the CdS/ZnS/ZnO system studied in this paper, selective substrate activation allows control over nucleation while the growth of each component can be controlled by many factors, in particular TU concentration and presence of ethanol. In addition, the concentration of ammonia/MEA is important insofar as too much complex will prevent ZnO deposition while too little will lead to excessive precipitation in solution. An example of the importance of interactions between different solution species is shown by the role of Cd^{2+} in tying-up sulfide ion as it forms, preventing formation of ZnS in the early stages of deposition, as was suggested in the Results section dealing with the effect of Cd on the deposition. This changes the initial deposition on activated (for ZnO) substrates from CdS to ZnO (+ varying amounts of CdS depending on other conditions). The continuation of the deposition, when CdS often becomes a major component, depends on how much ZnO succeeds in growing, which is determined by the amount of uncovered (by CdS) ZnO deposit as well as by the amount of Zn^{2+} remaining in solution.

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Supporting Information Available: SEM cross-sectional micrographs of: various ZnO films deposited using a MEA/ammonia deposition bath (no Cd or TU); spurious ZnO precipitate attached to a non-activated film; various ZnO/CdS films on FTO glass using in situ activation; various ZnO/CdS films deposited using $KMnO_4$ activation. Scheme showing effect of Cd^{2+} on the deposition. This material is available free of charge via the Internet at http://pubs.acs.org.