Reproducible Chemical Bath Deposition of ZnO by a One-Step Method: The Importance of "Contaminants" in Nucleation

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Chemical bath deposition (CBD)[1] is one of the simplest methods for depositing semiconductor and ceramic films. All that is needed is a (usually) aqueous solution made up of a few common chemicals and the substrate on which deposition is required. However, CBD often suffers, perhaps more than most chemical processes, from lack of reproducibility. This is particularly true for ZnO films grown from alkaline solutions onto glass (one of the most commonly used substrates), unless a previously deposited seed layer, most often ZnO grown by a different method, is present. In fact, such seed layers are the norm for CBD ZnO deposition.[2–6] Attempts to grow ZnO directly on glass (and some other substrates), lead in most cases to no growth or to irreproducible and heterogeneous growth, and in cases where growth was found to occur, the deposition parameters were very narrow.[7,8] Several groups have pointed out that in the absence of seed layers, only scattered ZnO deposits are formed on various substrates.[5,8,9] Examples of seed layers other than ZnO that have been used are Au or Ag layers,[6,10,11] and functional monolayers.[12,13] The seed layers also promote columnar growth (the type of growth often preferred).

We found that CBD of ZnO, using mixed ethanolamine/ammonia complexation of the Zn, proceeded reliably and reproducibly using a particular bottle of ethanolamine (designated here as impure-EA), but little or no deposition occurred using various other bottles of the same reagent (designated here as pure-EA). As described below, we traced this difference to the presence of contaminants in the impure-EA. The purpose of this letter is 2-fold: to demonstrate how small amounts of contaminants can strongly affect CBD processes by forming in situ nucleation centers and to exploit this knowledge to facilitate CBD of ZnO in the absence of a predeposited seed layer, in a more reproducible manner, and less dependent than usual on solution composition.

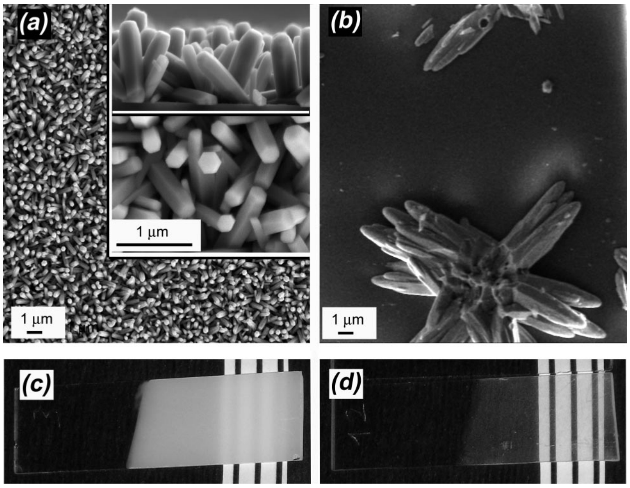

Figure 1. (a) SEM image of a typical ZnO film deposited on glass using impure-EA. The insets show higher magnification views. Upper inset: cross section. Lower inset: plan view. (b) Plan view SEM image of ZnO film using pure-EA. (c, d) Visual images of similar films as in images a and b, respectively. The black and white lines below the samples are to enhance visualization.

Figure 1a shows a typical ZnO film (verified by XRD to be wurtzite ZnO) obtained on glass using the accidentally contaminated impure-EA, while 1b shows a typical very sparse ZnO deposit formed in the same way, but using uncontaminated pure-EA. Images c (impure-EA) and d (pure-EA) in Figure 1 show the visual appearance of similar films. Deposition from contaminant-free solution is not reproducible: the film in Figure 1d is visually better than normal. Such microscopically inhomogeneous films only form at low ammonia concentrations. Many such depositions produce no visible deposit whatsoever, especially when a higher concentration of ammonia (where deposition from impure-EA reproducibly occurs) is used.

Inductively coupled plasma (ICP) elemental analysis of the EAs revealed the presence of 15 ppm Fe in the impure-EA (equivalent to 1.5 ppm Fe in the deposition solution) compared to 0.04 ppm in the pure-EA.

Intentional addition of aqueous solutions of Fe compounds, either Fe^{2+} or Fe^{3+} (as ferrous ammonium sulfate or ferric chloride} at concentrations between 0.5 and 10 ppm to the deposition solution containing pure-EA resulted in formation of ZnO films of fair (although not very good) homogeneity, as well as not very dense (Figure 2a), together with copious precipitation of ZnO in the deposition solution. (Among different ions tried instead of Fe, only Mn^{2+} ($MnCl_2$) was effective and in fact gave more homogeneous films than did Fe (Figure 2b).)

These films are a large improvement on those obtained using the pure-EA/ammonia bath in the absence of any

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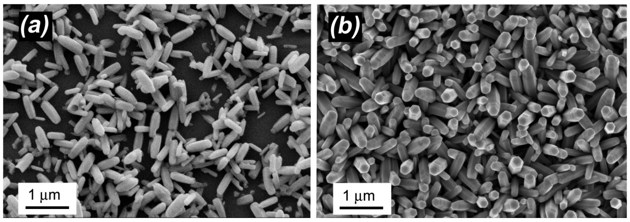

Figure 2. SEM images of ZnO films deposited from pure-EA based deposition solutions intentionally contaminated by (a) 1 ppm Fe^{3+}, (b) 1 ppm Mn^{2+}. In both cases, solutions of the contaminants were added directly to the deposition solution.

"contaminant". However, they are still considerably less reproducible and usually less homogeneous than those deposited using the impure-EA. To investigate this difference, we added Fe salts to pure-EA, rather than directly to the deposition solution, in an attempt to obtain the form of Fe found in the accidentally contaminated impure-EA. The procedure, arrived at by trial and error, and that was found to give similar results to the original contaminated impure-EA is described in the Supporting Information. We designate this intentionally contaminated EA as EA:Fe.

It is important to stress that, among the hundreds of experiments carried out by us, all films deposited using contaminated EA, whether deliberately contaminated (EA:Fe) or accidentally contaminated (inpure-EA), were reproducibly good while in not a single case were even slightly comparable films obtained in the absence of contamination. In parallel with the film deposition, ZnO precipitation occurred in the case of contaminated deposition while little or no precipitation occurred using noncontaminated solutions.

The reason for the beneficial effect of the Fe (or Mn) is probably related to the formation of in situ nucleation centers by metal-containing species. When the metal salts are added to the deposition solution, they can form hydrated oxide colloids, such as FeOOH or MnOOH. Fe and Mn oxides are well-known to adsorb heavy metal ions.[14] (Fe oxides in particular are used to purify water.[15]) We suggest that the Fe and Mn oxide colloids act as nucleation centers for ZnO growth. Those colloids, whether formed or adsorbed on the substrate, promote film growth, whereas the greater part of the colloid in the solution results in ZnO growth and subsequent precipitation from the solution. Although we are unable to identify the specific oxide or hydroxyoxide involved, it is likely that all (hydroxy)oxides of Fe or Mn are active as nucleation centers.[16] For example, we note that deposition of ZnO has been shown to occur directly onto Fe_3O_4 particles without the need for any seed layer.[17]

Good-quality, thick ZnO films (images b and c in Figure 3) of ZnO are formed if the substrate is immersed first in a bath containing impure-EA or EA:Fe just long enough until a ZnO film becomes visible (Figure 3a), and then well-rinsed and immersed in a bath made from pure-EA. Thus films grow efficiently from noncontaminated pure-EA bath once the nucleation has been successfully initiated. This is an important indicator of the effect of Fe as a nucleation center. In this particular experiment, the initial deposition in the contaminated bath is another way of forming a seed layer, normally used in ZnO deposition. For the more general case described in this study, (when Fe is present in the solution) however, the seed layer is formed in situ rather than as a separate step. Additional support for the effect of Fe as a nucleation center is provided by the fact that that good ZnO films can be grown from the present solution in the absence of contaminants onto glass substrates covered with Au nanoislands: We noted above the previous use of Au as seed layers for ZnO growth.[6]

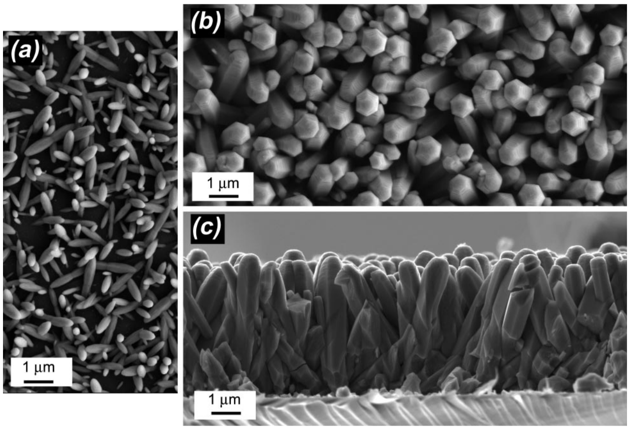

Figure 3. SEM images (a) ZnO seed layer grown using impure-EA; (b) plan view and (c) cross-section view of ZnO film grown from contaminant-free pure-EA solution on this seed layer.

To further support the above hypothesis of the role of metal oxides as nucleation centers, deposition was carried out but in the absence of Zn. The following observations (only valid if the solution was heated to the deposition temperature of 75−90 °C) were made: The deposition solutions containing impure-EA or EA:Fe became slightly opaque with a noticeable yellow-brown tint upon heating. (This also occurred for Fe or Mn ions added directly to the deposition solution using pure-EA). A visible difference in reflectivity was observed between the bottom half of the substrate that was immersed in the solution and the upper part (after drying). If the substrate is kept in such Fe-contaminated, Zn-free deposition solution for at least 30 min, some deposition can be seen by SEM (see the Supporting Information, images a and b in Figure SI-1); If a high concentration of Fe is used (>5 ppm in the final solution), a brownish tint on the glass can be seen by the naked eye (no XRD peaks could be observed from this deposit). Finally, X-ray photoelectron spectroscopy (XPS) of this deposit showed a broad Fe peak consistent with Fe(O)OH. These observations all show that a Fe hydroxy-oxide solid phase forms on the substrate.

Very good, dense ZnO films grow on these treated substrates from pure-EA solution (see the Supporting Information, c and d in Figure SI-1). This occurs on glass treated with Zn-free, Fe-containing solution for ≥ 30 min as well as on glass treated for 10 min, on which no visible—even in SEM imaging—Fe hydroxy-oxide films are formed.

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The reason for the superiority of the Fe-treated EA process compared to the direct addition of Fe ions to the deposition solution is probably due to the more gradual formation of the nuclei in the former case, which is a result of the formation of an EA-Fe hydrated complex. (We believe that the slow gelation of EA upon addition of Fe^{2+} (see the Supporting Information) is a result of the formation of this complex.[18]) This complexation favors slow formation of small iron oxide colloids, rather than the more rapid precipitation of larger particles that occurs upon direct addition of Fe salts to the deposition solution. These larger clusters of iron hydroxy-oxide will be less active than smaller colloids (less tendency to adhere to the substrate) and will also precipitate out more rapidly, as observed.

The influence of Fe and Mn "contaminants", whether for good or for bad, on the CBD of ZnO is not limited only to the present bath chemistry but is much more general. The beneficial effect of enhanced nucleation on the substrate is most pronounced when EA is used as a complex. However, some improvement is found for deposition (on glass) from different baths, as long as no seed layer was present. If a seed layer is present, the deposition is worse, because homogeneous nucleation in the solution increases. Thus the effect of the contamination depends strongly on other deposition parameters (solution, substrate). Of particular importance, in contrast to ZnO deposition in general, the solution parameters that gave good films were wide (e.g., deposition was possible between pH 9−12 and using many different Zn salts). In view of our results, we propose that problems of nucleation are often the cause for lack of reproducibility and narrow deposition parameters in ZnO deposition.

Crystal size and film density can be controlled to some extent by varying "contaminants" and ammonia concentration as well as the bath temperature. For example, high "contaminant" concentration will favor less dense films and smaller diameter crystals as a result of faster consumption of Zn ions because of faster homogeneous formation and precipitation of ZnO powder and/or a different distribution of iron oxide particles on the substrate. Lower concentration of ammonia, which serves as Zn^{2+} complexing agent, has the same effect, again because of faster homogeneous formation and precipitation of ZnO powder.

Finally, in the context of identifying reasons for lack of reproducibility in CBD processes and directly connected to the discussion in the previous paragraph, we found that, during routine laboratory use of a 1 L bottle of ammonia, the concentration of ammonia was reduced by 20−25%. Although this is not surprising, it needs to be pointed out, because we believe that most researchers do not take it into account and ammonia is one of the most frequently used CBD reagents.

In conclusion, we have demonstrated how impurities in CBD solutions can be critical in determining deposition, in the present case by facilitating film nucleation. Additionally, we have exploited this fact to develop a novel reliable method for a one-step ZnO deposition over a relatively wide range of solution parameters on various substrates.

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Supporting Information Available: Figure SI-1. SEM images of Fe hydroxy-oxide deposits on glass and ZnO films (both plan view and cross section) grown on these deposits. Experimental details of the ZnO deposition, including the procedure for addition of Fe compounds to ethanolamine (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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