

## Sol-gel synthesis of ZnO transparent and conductive films: A critical approach

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### ABSTRACT

The main aspects of the sol-gel synthesis of ZnO thin films were critically examined with particular reference to the optimization of the process parameters that influence specific properties of the films, such as the transparency, the crystallization behavior and the electrical resistivity. Starting from zinc acetate dihydrate, anhydrous ethanol and triethanolamine, a valuable sol-gel route was set. This route allowed the preparation of transparent ZnO thin films by dip-coating. Triethanolamine, thanks to its high chelating efficiency towards  $\text{Zn}^{2+}$ , permitted to prepare stable zinc acetate dihydrate solutions wholly at room temperature. The structural, optical and morphological characteristics of the films were examined by glancing incidence X-ray diffraction, UV-vis spectroscopy and atomic force microscopy. Single layer films, with a thickness of about 120 nm, characterized by a high adhesion force (about  $140 \text{ Kg cm}^{-2}$ ), were obtained. The crystallization behavior of dip-coated amorphous films was explored in the 500–600 °C range; polycrystalline films, formed by randomly oriented ZnO nanocrystals (about 20 nm), with an average transmittance higher than 90% in the visible region, were obtained. Finally, a strong influence of annealing environment on electrical resistivity was observed.

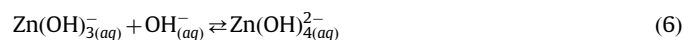
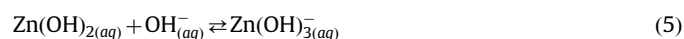
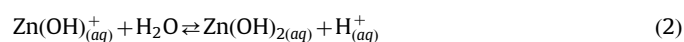
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### 1. Introduction

Transparent conducting oxides (TCOs) are extensively used as part of numerous electronic and optoelectronic devices like TFT, sensors and solar cells [1–5]. In particular, they play an irreplaceable role in thin film photovoltaic devices where both conductive front and back electrodes, as well as intermediate layers, exhibiting either transmitting or reflecting behavior, are needed [6–10]. Among others, due to its high transmittance and low resistivity, tin doped indium oxide (ITO) has been often preferred as front electrode. However, indium is somewhat rare and really expensive. Moreover, care must be taken when exposing  $\text{SnO}_2$  to hydrogen plasma atmosphere in order to avoid degradation of optical and electrical properties. Recently, doped zinc oxide (ZnO), due to its lower cost, wide availability, non-toxicity and stability, is prevailing as suitable alternative to ITO based TCO films. Typical doping elements used to prepare doped ZnO thin films include Al [11–14], B [15–17], Ga [18], In and Sn [19–22].

The synthesis of ZnO films by means of evaporation techniques has reached a solid level of knowledge [23,24]. The sol-gel route

has been proposed as a cost-effective alternative to vacuum-assisted deposition techniques. It is a low temperature wet chemical process that is characterized by a very high versatility. In fact, it allows controlling chemical composition, shape, structure, textural and morphological properties of final materials by adjusting processing parameters. Moreover, sol-gel allows coating large area of arbitrary shaped substrates. The key aspect of any wet synthesis of ZnO is the simultaneous control of the hydrolysis equilibrium of  $\text{Zn}^{2+}$  and the solubility equilibrium of  $\text{Zn}(\text{OH})_2$ . The formation of zinc oxide in aqueous environment can be described by the following reactions [25].



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Equilibrium (3) is strongly shifted towards right ( $K \sim 10^6$ ) as a consequence of the very low solubility in water of  $\text{Zn}(\text{OH})_2$  ( $K_{sp} = 3.5 \times 10^{-17}$  at 25 °C), therefore it is not easy to hydrolyze  $\text{Zn}^{2+}$  without precipitation of zinc hydroxide. On the other hand, it is evident that the above equilibria are strongly influenced by the pH value at 25 °C. In acidic conditions ( $\text{pH} < 6$ ),  $\text{Zn}^{2+}$  is the main ion present in solution; in neutral or slightly basic conditions the most part of Zn is present as solid  $\text{Zn}(\text{OH})_2$  or ZnO because both of them have very low solubility in this range of pH; at pH 12 or above, the main zinc specie is  $\text{Zn}(\text{OH})_4^{2-}$  [25].

Since the sol–gel synthesis of ZnO involves the preparation of a colloidal solution of a molecular precursor of Zn that is then hydrolyzed, thus producing oxo-hydroxylated species whose polycondensation originate the Zn-oxo colloidal particles, the problem of avoiding the precipitation of  $\text{Zn}(\text{OH})_2$  is crucial. Different approaches have been proposed to solve this problem, they have been well-reviewed in two recent papers [26,27].

Spanhel and Anderson [28], for the first time, have successfully prepared a stable colloidal solution of ZnO starting from a diluted solution (about 0.1 M) of zinc acetate dihydrate [ZAD:  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ] in absolute ethanol [EtOH:  $\text{CH}_3\text{CH}_2\text{OH}$ ], using drastic conditions (reflux at 80 °C for 180 min) followed by the addition of a well defined amount of lithium hydroxide hydrate ( $\text{LiOH} \cdot \text{H}_2\text{O}$ ). Afterwards, many variations of such a procedure, concerning both different process parameters and different solvents and complexing agents, have been presented. Ohyama et al. [29,30] starting from the same precursor, ZAD, have achieved a more concentrated solution,  $[\text{Zn}^{2+}] = 0.6$  M, because they had used an alcohol of high molecular weight as solvent, 2-methoxyethanol [2-ME:  $\text{CH}_3\text{O}(\text{CH}_2)_2\text{OH}$ ] and two complexing agents of  $\text{Zn}^{2+}$ : monoethanolamine [MEA:  $(\text{HOCH}_2\text{CH}_2)\text{NH}_2$ ] and diethanolamine [DEA:  $(\text{HOCH}_2\text{CH}_2)_2\text{NH}$ ]. This procedure has allowed to prepare the homogeneous solution of the precursor in milder conditions (30 min at 60 °C), from which ZnO films were obtained. The mean thickness of a single layer film was about 40 nm. A wide concentration range of the  $[\text{Zn}^{2+}]$ , ranging from 0.05 to 1 M, was explored by Znaidi et al. [31,32], using ZAD as precursor, EtOH and 2-ME as solvents, MEA, triethanolamine [TEA:  $(\text{HOCH}_2\text{CH}_2)_3\text{N}$ ] and lactic acid as complexing agents. The hydrolysis was carried out both in drastic (refluxing at 80 °C for 120–180 min) and mild (120 min at 60 °C) conditions. From the above solutions ZnO films were obtained by spinning or dip-coating. In this case the mean thickness was about 20 nm for a single layer. Kim et al. [33] employed isopropanol [*i*-PrOH:  $(\text{CH}_3)_2\text{CHOH}$ ], a solvent with a boiling point lower than 2-ME, and MEA to prepare ZAD solutions with different  $[\text{Zn}^{2+}]$ , ranging from 0.3 to 1.3 M that were hydrolyzed at 50 °C for 60 min. O'Brien et al. [34–36] prepared ZnO films by employing a sol–gel route similar to the one proposed by Kim et al. [33] but starting from a different Zn molecular precursor: the anhydrous zinc acetate. After a single coating step, according to the initial  $[\text{Zn}^{2+}]$  concentration, ranging from 0.3 M to 1.3 M, films with different thickness were obtained (from 84 nm to 437 nm). The transparency of these films in the UV–vis range was found to be strongly affected by the thickness [34]. Dutta et al. [37] starting from ZAD, *i*-PrOH and DEA, achieved ZnO films from highly diluted solutions,  $[\text{Zn}^{2+}]$  ranging from 0.03 to 0.1 M, but hydrolyzed at room temperature. Tsay et al. [38] have employed EtOH and MEA to prepare ZAD solutions with  $[\text{Zn}^{2+}] = 0.75$  M that were hydrolyzed at 60 °C for 120 min. So ZnO films were obtained by spin-coating.

From this overview, it is evident that the control of the hydrolysis and solubility equilibria, Eqs. (1)–(4), has been obtained by the combined effect of complexing agents and temperature.

This work reports a methodical study aimed at a deeper understanding of the influence of the different synthesis conditions on the final properties of transparent sol–gel ZnO thin films, with particular reference to the optimization of the process parameters that affect the specific ZnO film properties for photovoltaic (PV)

applications, such as the transparency, the thickness and the electrical resistivity.

## 2. Experimental details

### 2.1. Materials

All reagents were used as received. Zinc acetate dihydrate (ZAD 99.999% purity), acetic acid (HAc:  $\text{CH}_3\text{COOH}$ ), and triethanolamine (TEA 98% purity) were purchased from Sigma-Aldrich. Anhydrous ethanol (EtOH) was provided by Fluka.

### 2.2. Films preparation and processing

Sol–gel ZnO thin films were deposited on glass substrates (Corning 1737) by dip-coating. These substrates are alkaline earth boro-aluminosilicate glasses with softening ( $10^{7.6}$  poise) and strain ( $10^{14.5}$  poise) points at 975 and 666 °C, respectively.

Different stock solutions were prepared by dissolving a proper amount of ZAD in EtOH followed by the addition of a suitable amount of additive, HAc or TEA, in such a way that the molar ratio between Zn and the complexing agent was kept constant at 1. They were hydrolyzed at room temperature for 1 day before film deposition. Composition, molar concentration and pH of ZAD stock solutions in anhydrous ethanol with the related labels are listed in Table 1. All stock solutions are stable and homogeneous. Their chemical stability range from one to two months increasing the TEA amount.

The films were prepared at room temperature by means of a KSV dip-coater. The glass substrates were dipped into the stock solution and withdrawn at 10 mm/min. The films were first dried in air atmosphere at 100 °C for 2 h and then subjected to different heat-treatment. Some selected films were post-annealed in nitrogen or forming gas (mix,  $\text{H}_2$  2% – Ar balance) flux at 250 °C for 0.5 h. The heating rate of 10 °C/min was selected to reach the set point temperature. Annealing temperature, time and environment to which the studied films have been subjected are displayed in Table 2.

In order to improve film adhesion, glass substrates were subjected to chemical treatment to modify surface wettability. Water contact angles (WCA) of the glass surfaces before and after several chemical etching were measured using a Dataphysics OCA 20.

### 2.3. Films characterization

Before each characterization, the film deposited on one face of the glass substrate was removed by an HCl etching.

The film adhesion was tested by means of the Z-axis pull stud method thanks to a Sebastian Five-A instrument. The film thickness was measured by a KLA Tencor P-10 surface profiler. At least three scans were collected for each sample, both up- and down-

**Table 1**

Composition, molar concentration and pH of ZAD stock solutions in anhydrous ethanol with the related labels.

Stabilizers	Stock solutions					
	S0					
HAc		S1				
TEA		S2	S3	S4	S5	S6
<b>Concentration</b> ( $\text{mol} \cdot \text{L}^{-1}$ )	0.12	0.50	0.60	0.75	1.0	1.2
<b>pH</b>		4.7				
	6.5	6.8	7.1	7.4	7.6	7.8

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