# Seed-Layer Free ZnSnO3 Nanowires

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$ZnSnO_3$ semiconductor nanostructures have several applications as photocatalysis, gas sensors, and energy harvesting. However, due to its multicomponent nature, the synthesis is far more complex than its binary counter parts. The complexity increases even more when aiming for low-cost and low-temperature processes as in hydrothermal methods. Knowing in detail the influence of all the parameters involved in these processes is imperative, in order to properly control the synthesis to achieve the desired final product. Thus, this paper presents a study of the influence of the physical parameters involved in the hydrothermal synthesis of $ZnSnO_3$ nanowires, namely volume, reaction time, and process temperature. Based on this study a growth mechanism for the complex Zn:Sn:O system is proposed. Two zinc precursors, zinc chloride and zinc acetate, were studied, showing that although the growth mechanism is inherent to the material itself, the chemical reactions for different conditions need to be considered.

Keywords: ZnSnO3 ; Nanowires ; Hydrothermal synthesis ; ZTO

## 1. Introduction

As a result of its impressive multifunctionality, ZnO-based thin-films and nanostructures have received a lot of attention in the last decade [1][2][3]. While ZnO on its own captured a large interest, doping or mixing with other binary compounds brings a new level of possibilities, as the material properties can be improved/tailored to different applications depending on the cationic ratio. This has been widely explored in oxide thin-films, for example with zinc-tin oxide (ZTO) [4][5]. ZTO structures crystalize by solid-state reaction in the stable inverse spinel ortho-stannate $Zn_2SnO_4$ phase or in the metastable $ZnSnO_3$ phase, either in perovskite (orthorhombic, orth, or face centered, fcc) or rhombohedral forms [6][7][8][9]. $ZnSnO_3$ is a ferro/piezoelectric material with a high polarization along the *z*-axis (~59 μC/cm$^2$) which is much higher than that of ZnO (~5 μC/cm$^2$) [10][11][12][13][14]. Its band-gap of 3.9 eV is higher than that of $Zn_2SnO_4$ [15][16].

While vapor phase processes can be used to synthesize high-quality ZTO nanostructures [17][18], these are expensive, cumbersome and require high temperatures (>700 °C). The demand for low-cost processes compatible with flexible substrates requires solution processes that allow for the synthesis of nanostructures at low-cost, using simple and easy methods, ideally upscalable to industrial-scale quantities [19].

## 2. Seed-Layer Free Hydrothermal Synthesis of $ZnSnO_3$ Nanowires

The multicomponent nature of ZTO makes the synthesis process quite challenging, given the different ionic sizes and diffusivity of the cations. Furthermore, each ZTO structure has different nucleation and growth times and requires a specific range of synthesis temperature [20]. In literature it has been shown the possibility to control the shape and type of the nanostructures and consequently the electrical, optical, and mechanical properties, by controlling the chemical and physical parameters of the synthesis [7][21][22].

In this study, $ZnSnO_3$ nanowires were synthesized via hydrothermal method in a conventional oven [23][24]. Briefly, the ZTO hydrothermal synthesis was performed by dissolving zinc chloride, $ZnCl_2$, (or zinc acetate, ZnAc) and tin chloride ($SnCl_4{\cdot}5H_2O$) separately in deionized water and then mixing these solutions. The surfactant ethylenediamine (EDA) was then added and stirred for 30 min, after which the mineralizer sodium hydroxide (NaOH) was added. The solution was then transferred into an autoclave and kept in an electric oven varying the temperature and the reaction time. The final product comprising the nanostructures was alternately washed with deionized water and isopropyl alcohol and centrifuged. After washed, the nanostructures were dried at 60 °C, in vacuum. Aiming to study the influence of the chemico-physical parameters in the ZTO nanostructures growth, the conditions showed in Table 1 were tested. This work was conducted without employing any seed-layer in the synthesis of ZTO nanostructures; hence, the obtained structures depend exclusively on the chemico-physical parameters of the synthesis. Moreover, the obtained nanostructures are in powder form, which through a variety of transfer methods allow for a higher degree of freedom for integration on different substrates, without contamination from the seed-layer material [25][26].

Table 1 – Conditions studied to optimize the hydrothermal synthesis of $ZnSnO_3$ nanowires.

| Zinc precursor | NaOH molar concentration (M) | $H_2O$:EDA volume ratio (mL:mL) | Total volume (mL) | Synthesis duration (h) | Synthesis temperature (°C) |
|---|---|---|---|---|---|
| ZnAc; $ZnCl_2$ | 0.1; 0.24; 0.5 | 15:0; 9:6; 8:7; 7.5:7.5; 7:8; 6:9; 0:15 | 7.5; 11; 15 | 2; 8; 12; 18; 24; 36; 48 | 150; 180; 200; 220 |

## 3. Influence of Chemico-physical Parameters of the Synthesis in the $ZnSnO_3$ Nanowires Growth

Two zinc precursors were used in this study and their solubility in the surfactant (EDA) showed to be one of the critical parameters to optimize the synthesis of the $ZnSnO_3$ nanowires. Comparing the tin precursor solubility in EDA with the zinc precursors' solubility it was possible to conclude that the lower solubility of ZnAc favors tin-based structures while the higher solubility of $ZnCl_2$ promotes zinc-based structures. This results in different optimal values of Zn:Sn molar ratios, for each of these two precursors. Furthermore, using $ZnCl_2$ as zinc precursor results in larger and significantly more homogeneous nanostructures (less mixture of phases/structures) and more reproducible reactions, which is due to its higher solubility, promoting a faster evolution of the species in synthesis. As directing growth agent, the surfactant has crucial role to achieve the nanowire form. Similarly to what is observed for the NaOH concentration, the EDA concentration influences the solution's pH which favors the formation of either tin-based structures (lower concentrations) or zinc-based structures (higher concentrations). The growth of $ZnSnO_3$ nanowires was achieved for intermediate values only, proving that both EDA and NaOH optimal concentrations are a compromise between the role they play in the synthesis and their influence on the pH [23].

$ZnSnO_3$ is achievable for more energetic syntheses, i.e., under higher pressure (higher volume), while for lower energetic processes the more energetically stable phases ($Zn_2SnO_4$ and $SnO_2$) are obtained. It was observed that at least 12 h of synthesis at 200 °C were necessary to predominantly obtain nanowires, while very long synthesis (36 h), or at higher temperatures (220 °C) result in the decomposition of the $ZnSnO_3$ phase into $Zn_2SnO_4$ and $SnO_2$ [24].

The optimal conditions to achieve the $ZnSnO_3$ nanowires were a Zn:Sn molar ratio of 2:1 (1:1) using $ZnCl_2$ (ZnAc) as zinc precursor, a NaOH concentration of 0.24 M with a $H_2O$:EDA volume ratio of 7.5:7.5 mL:mL for syntheses at 200 °C for 24 h (Figure 1). This shows the viability of the hydrothermal process to achieve a metastable ZTO phase at low temperatures, provided that proper control of the synthesis parameters exists.

Figure 1 – $ZnSnO_3$ nanowires produced using as zinc precursor (a) $ZnCl_2$ and (b) ZnAc. From reference [24].

## 4. Properties and Applications

The $ZnSnO_3$ nanowires achieved were characterized concerning their optical, electrical and piezoelectrical properties, resulting in electrical resistivity (measured in vacuum inside SEM) of 1.4 kΩ·cm, optical band-gap of 3.6 eV and piezoelectric constant of 23 pm/V [23][27]. These properties allow to envisage application on numerous next-generation nanoscale devices such as nanogenerators (reported in [27]), sensors, photocatalysis, solar cells, resistive switching memories, and transistors [18][28][29][30][31][32][33][34].

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