Synthesis of \( \text{Zn}_2\text{SnO}_4 \) Powders via Hydrothermal Synthesis for Ceramic Targets

Abstract

The synthesis of \((\text{SnO}_2)_x(\text{ZnO})_{1-x}\) particles as a ceramic target material use for thin film production via hydrothermal technique within a broad range of \(x\) values \((x=0-1)\) was investigated. The phase formation of the \((\text{SnO}_2)_x(\text{ZnO})_{1-x}\) system \((x=0-1)\) was mapped in terms of changing \(x\) values. \(\text{Zn}_2\text{SnO}_4\) almost pure phase forms as \(x=0.29\) for the \((\text{SnO}_2)_x(\text{ZnO})_{1-x}\) composites at 220\(\degree\)C for 24h under hydrothermal conditions. The synthesised \(\text{Zn}_2\text{SnO}_4\) powder, as a target, exhibits suitable properties in terms of an adequate electron concentration and high mobility of free charge carriers. The obtained results show that ceramic targets synthesized via hydrothermal synthesis are candidate material for use in thin film transistor channel.

1. Introduction

Zinc stannate (ZTO) composite powder is a candidate target material that can be used in a wide variety of applications, such as gas and humidity sensors, transparent thin film transistors (TFT-T) [1], transparent conductive electrodes, functional coating and as negative electrodes for Li-ion batteries [2]. ZTO is an n-type ternary oxide semiconductor (II–IV–VI) that has unique properties, including high electron mobility, high electrical conductivity, low visible absorption and excellent optical properties [3]. Synthesis of zinc stannate composite powders has been investigated via different techniques, including solid state reaction, thermal evaporation, sol–gel, solid state reaction, coprecipitation and hydrothermal synthesis [4–7]. However, hydrothermal synthesis of \((\text{SnO}_2)_x(\text{ZnO})_{1-x}\) \((x=0-1)\) particles has not been reported in detail. Hydrothermal synthesis has advantages among the other powder synthesis techniques to produce high purity and controlled particle size and morphology. Particle physical properties can be easily controlled by adjusting synthesis temperature, time and initial concentration of cations. In addition to that, the hydrothermal method is environmentally friendly and energy efficient process due to produce oxide materials directly without any extra process step, including calcinations or milling [8]. The research objective of this study were to investigate the hydrothermal synthesis of \((\text{SnO}_2)_x(\text{ZnO})_{1-x}\) nanocomposite powder within a broad range of \(x\) values \((x=0-1)\) and to evaluate phase development and particle characteristics of \(\text{Zn}_2\text{SnO}_4\).

2. Experimental Procedure

Zinc nitrate \((\text{Zn(NO}_3)_2\cdot6\text{H}_2\text{O})\) and tin tetrachloride \((\text{SnCl}_4\cdot5\text{H}_2\text{O})\) salts were used as precursors. Zinc nitrate and tin tetrachloride were dissolved into distilled water separately to form two transparent solutions. After two solutions were mixed under stirring, \(\text{NH}_4\text{OH}\) solution was added dropwise into the solution of \(\text{Zn}-\text{Sn}\) mixture. As white precipitates form at pH 8.0, supernatant solution was centrifuged at 5000 rpm for 5 minutes to
remove dissolved anions. Before feeding of the Zn-Sn mixture into the hydrothermal reactor, the pH of the suspension was adjusted to 8.0 by deionized water. The hydrothermal reaction was conducted at 220\(^\circ\)C for 24 h at 60\% degree of filling under autogenous pressure. As the hydrothermal reaction was completed, the product was washed with distilled water for several times and dried in an oven at 90\(^\circ\)C overnight. The phase development of the composite powder was analysed by the XRD method (Rigaku Co., Ltd., Japan). Particle characteristics, including particle size and distribution and morphology were investigated by SEM (Zeiss Supra 50V, Germany) and STEM (JEOL 2100F, FEI, 200kV HRTEM, Japan). The microstructure of the Zn\(_2\)SnO\(_4\) samples was evaluated by SEM. The average grain size of sintered target was calculated by ImageJ.

A target with a diameter of 40mm was prepared from hydrothermally synthesized Zn\(_2\)SnO\(_4\) powder by pressing at 200MPa in a cylindrical die and sintering at 1200 \(^{\circ}\)C for 2 h. Deposition of the films from the Zn\(_2\)SnO\(_4\) target was achieved by AC magnetron sputtering equipment from INFICON. Sputtering was carried out on the glass and silicon substrates in an ambient atmosphere of pure argon for 5 h. Thin films prepared by AC magnetron sputtering were characterized by Hall measurements via the Vander-Pauw method in a magnetic field induction of 0.63 Tl.

3. Results and Discussions

3.1. Phase formation of (SnO\(_2\))\(_x\)(ZnO)\(_{1-x}\) (x=0-1)

The phase formation of the (SnO\(_2\))\(_x\)(ZnO)\(_{1-x}\) nanocomposite system was investigated the range of x (0.0, 0.05, 0.1,..., 0.8, 0.9, 1.0) under hydrothermal synthesis conditions at 220\(^\circ\)C for 24h. The XRD patterns of the synthesized powders with x=0.05, 0.1, 0.2 are given in Figure 1. Zn\(_2\)SnO\(_4\) phase was formed mainly with minor ZnO precipitates at x=0.2.

![Figure 1. XRD pattern of hydrothermally synthesized (SnO\(_2\))\(_x\)(ZnO)\(_{1-x}\) powders prepared with x=0.05, 0.1, 0.2 at 220\(^\circ\)C.](image)

The calculation of the molar ratio of (SnO\(_2\))\(_x\)(ZnO)\(_{1-x}\) showed that the x value should be 0.33 for the formation of the pure Zn\(_2\)SnO\(_4\) stable phase. However, small amount of SnO\(_2\) was formed at x=0.33 with Zn\(_2\)SnO\(_4\) major phase. The formation of SnO\(_2\) at x=0.33 can be clarified that precipitated ZnO removed from the system during centrifugation. The supernatant solution was analyzed by ICP-OES to determine the amount of soluble Zn\(^{2+}\) and Sn\(^{4+}\) cations. The results showed that while the Sn\(^{4+}\) cation concentration was less than 5.29 ppb, the concentration of Zn\(^{2+}\) was approximately 4000 ppm. This result proved the removing of ZnO during washing process before charging of the solution to the reactor. Therefore, extra Zn\(^{2+}\) cations (0.04\% by mass) should be added to prepared solution to obtain pure Zn\(_2\)SnO\(_4\) without any residual phases as SnO\(_2\). XRD pattern of (SnO\(_2\))\(_x\)(ZnO)\(_{1-x}\) x=0.29 are given in Figure 2. The obtained Zn\(_2\)SnO\(_4\) powders were heat treated at 800\(^\circ\)C to examine the excess crystallization of SnO\(_2\). After heat treatment, no SnO\(_2\) phase observed.
Figure 2. XRD pattern of hydrothermally synthesized (SnO$_2$)$_x$(ZnO)$_{1-x}$ powders prepared with $x=0.29$

Up to $x=0.7$, SnO$_2$ and Zn$_2$SnO$_4$ rich phases were identified. With increasing $x$ value ($x>0.7$), SnO$_2$ began forming as a major phase. The phase formation of the (SnO$_2$)$_x$(ZnO)$_{1-x}$ system in the full range ($x=0-1$) were mapped as showed in Figure 3. Whereas major phases are marked with green lines, minor phases are marked with yellow lines. The results revealed that solutions of the ZnO and SnO$_2$ binary phases were limited within each solution in the system. For $x=0.30-0.90$, the Zn$_2$SnO$_4$ and SnO$_2$ phases coexist. The single phase Zn$_2$SnO$_4$ occurs only at $x=0.29$ at 220°C for 24h.

Figure 3. Map of hydrothermally synthesized (SnO$_2$)$_x$(ZnO)$_{1-x}$ phases with respect to $x$ value at 220°C.

The TEM images and EDX results of the labelled particles prepared with $x=0.33$ are presented in Figure 4. The particle size is 40-50 nm with cubic morphology. The dark (Zn$_2$SnO$_4$) and light (SnO$_2$ rich) regions were numbered as 1 and 2, respectively in STEM images. The region 1 consists of 26% zinc and 13% tin, with the remaining amount as oxygen, while Region 2 contains 2% zinc and 14% tin, with the remaining amount as oxygen. TEM-EDS studies of the samples showed that there is very small amount tin rich regions even in $x=0.29$ samples. Therefore, the almost single phase of Zn$_2$SnO$_4$ formed at $x=0.29$.

Figure 4. STEM and EDS results of hydrothermally synthesized powders prepared with $x=0.33$ at 220°C.

3.2. Electrical properties of thin films prepared by AC magnetron sputtering from synthesized Zn$_2$SnO$_4$

The morphological property of powder used in target preparation was evaluated by SEM (Figure 5). Agglomerates are composed of spherical nanosize grains with average particle size 50-60 nm. SEM image of the sintered Zn$_2$SnO$_4$ target at 1200°C for 2h was shown in Figure 5. The average grain size of the sintered target was 1±0.5 μm and Zn$_2$SnO$_4$ target indicates the >92% of theoretical density. The films deposited from the Zn$_2$SnO$_4$ target, the concentration of electrons was 3.0x10$^{18}$ cm$^{-3}$ and mobility of free carriers was 15 cm$^2$/V.s. After thermal treatment for 1h at 400°C, the films became transparent (transparency was between 80-90%),
the concentration and mobility of free charge carriers were 1.8x10^16 cm^-3 and 20 cm^2/V.s, respectively. Thin films prepared from Zn2SnO4 powders can be used as channels of transparent thin film transistors (TTFT) [1]. A film, to be used for this purpose, must have a concentration of electrons from 10^15 cm^-3 up to 10^17 cm^-3 and be transparent. Therefore, these values meet the requirements for thin film transistor channel applications.

**Figure 5.** SEM images of (a) the hydrothermal synthesized Zn2SnO4 powder prepared with x = 0.29 at 220 ºC and (b) polished, thermally etched cross-section of the Zn2SnO4 target sintered at 1200 ºC for 2 h

4. Conclusion

In this study, hydrothermal synthesis of (SnO2)x(ZnO)1-x nanocomposite powder within a broad range of x values (x = 0–1) was investigated. Phase formations of the (SnO2)x(ZnO)1-x powder system in the range from x = 0.0 to 1.00 were mapped, and ZnO, SnO2 and Zn2SnO4 phases were found depending on the changing x value. The almost single phase Zn2SnO4 occurs only for x = 0.29 (Zn/Sn = 2:4:1) for the (SnO2)x(ZnO)1-x composite system at 220 ºC for 24 h. The obtained Zn2SnO4 powder, as a target, exhibits suitable properties in terms of an adequate electron concentration and high mobility of free charge carriers. The results show that the Zn2SnO4 powder synthesized by the hydrothermal method can be successfully used for thin film transistor channels. The results are particularly important to demonstrate that Zn2SnO4 powder synthesized by the hydrothermal method can be successfully used for thin films in different optoelectronics devices, for instance, as a channel in transparent thin film transistors.

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**References**