Effect of tin loading on physical properties and phase transformation of as-synthesized Zn-Sn-O compound powder synthesized by co-precipitation method

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Abstract

Zinc-Tin oxide compounds (Zn-Sn-O) were successfully prepared via a facile co-precipitation process using zinc dichloride dihydrate as the zinc source and tin tetrachloride pentahydrate as an additive source. The as-prepared product of Zn-Sn-O powders with various Sn additive contents (0-60 \%wt) were obtained without calcinations process. The effect of Sn additive on structural and microstructure properties of the samples were characterized by X-ray diffraction(XRD), scanning electron microscope(SEM). The results indicate that the crystallinity and morphologies of ZnO nanoparticles are significantly influenced by Sn additive. The phase formations of Zn-Sn-O including ZnO, ZnSn(OH)\textsubscript{6} were observed depending on the Sn-additive composition.

Keywords: Zinc oxide, Tin, Co-precipitation
1. INTRODUCTION

Zinc Oxide (ZnO) is typical n-type semiconducting material with wide direct optical band gap energy of 3.37 eV and large exciton binding energy of 60 meV [1]. It has been attracted great attentions in many practical applications such as transparent conducting electrode [2], gas sensor [3], UV-detector [4] and photodegradation [5]. However, due to its limitation of the optical and physical properties for specific applications, the incorporation with various elements, confinement in nanostructures and controlling of its morphologies could be the promising method for effective extension of its properties [6]-[8]. Recently, there have been a number of research works focusing on the effective method for the incorporation with Tin (Sn) into ZnO lattices. Ramin Yousefi and his group [9] gave the report on the physical and optical properties of Sn-doped ZnO nanobelts deposited using thermal evaporation method. The results indicated that the slight shift toward the larger diffraction angle of the diffraction peak of the Sn-doped ZnO nanobelts and their UV peaks was blue-shifted in comparison to pure ZnO nanobelts is effected by Sn-doping. Mi Jung and co-worker [10] employed chemical vapor deposition process to deposit Sn-doped ZnO nanowires with enhancement for green emission intensity. This phenomenon is due to excess oxygen vacancies caused by Sn-doping. Peng Song and his research group [11] successfully synthesized ZnSnO₃ hollow fibers using cotton as biotemplates with enhanced ethanol sensing.

In this work, we report the simple co-precipitation synthesis of as-synthesized Sn-Zn-O compound with various Sn loading exceeding 20 at.% into ZnO. The effect of Sn content on its physical properties was investigated using by X-ray diffraction (XRD) and scanning electron microscope (SEM).

2. EXPERIMENT

Zn-Sn-O compounds were synthesized by co-precipitation method using zinc dichloride [ZnCl₂] and tin tetrachloride pentahydrate [SnCl₄·5H₂O] as raw materials. In a synthesis process, 0.5 M of ZnCl₂ and 10-60 at.% of SnCl₄·5H₂O were dissolved in deionized water and further stirred for 1 h at room temperature. Then 50 ml of 0.5 M Sodium hydroxide (NaOH) solution was added into precursor solution until pH=14 was reached. The white colloid was obtained after this process and followed by washing until pH=7. As-prepared precipitates were dried at 80 °C for 24 h. White precipitates were grounded in a mortar for fine powder before characterization. Finally, Zn-Sn-O compounds with various Sn contents were obtained. The structural properties and morphologies of as-synthesized Zn-Sn-O powders were investigated by X-ray diffraction (XRD) technique and scanning electron microscope (SEM).

3. RESULT AND DISCUSSION

![XRD patterns of as-synthesized Zn-Sn-O compounds with difference Sn contents](image-url)

Fig. 1. XRD patterns of as-synthesized Zn-Sn-O compounds with difference Sn contents
The structural properties of Zn-Sn-O compound powders synthesized by co-precipitation method with different Sn contents were investigated by XRD and corresponding patterns are shown in Figure 1. The diffraction peaks situated at 2θ = 31.73°, 34.38°, 36.17°, 47.49° and 56.52° are ascribed to (100), (002), (101), (102) and (110) orientation planes with hexagonal wurtzite structure of ZnO (JCPDS File No. 76-0704), respectively. Moreover, the appearance of diffraction peaks positioned at 2θ = 22.90° 32.56° and 52.62°, which correspond to (200) (220) and (024) orientation plane of cubic phase ZnSn(OH)$_6$, respectively [12]. It is noticed that the diffraction peaks consisting the mixed phases of ZnO and ZnSn(OH)$_6$ are obtained after loading Sn toward 40 at.%. The possible formation mechanism of the pure ZnO via precipitation process using zinc dichloride (ZnCl$_2$) can be summarized by following reaction:

$$ZnCl_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaCl$$  

(1)

The intermediate product can be transform into ZnO by dehydration process as following reaction:

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$  

(2)

Meanwhile, with the incorporation of Sn by loading of SnCl$_4$, the possible co-precipitation reaction can be proposed as following equations:

$$2ZnCl_2 + SnCl_4 + 8NaOH \rightarrow Zn(OH)_6 + 8NaCl,$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

(3)

On the other hand, the vanishment of ZnO characteristic diffraction peaks occurs after loading Sn over 40 at.%, suggesting that the stocked precursor can be completely transformed into ZnSn(OH)$_6$ using co-precipitation reaction as following equation:

$$ZnCl_2 + SnCl_4 + 6NaOH \rightarrow ZnSn(OH)_6 + 6NaCl$$  

(4)

In addition, the significant shifts of peaks positions to larger angle are observed as Sn loading content increases, indicating the alternation of $d$-spacing of ZnO with specific Sn loading content. The interplanar $d$-spacing of the Zn-Sn-O compound powders could be calculated by Bragg's law equation as following equation:

$$2d \sin \theta = n\lambda$$  

(5)

Where $d$ is the lattice spacing, $n$ is an integer, $\lambda$ is the wavelength of incident x-ray CuK$_\alpha$ ($\lambda = 1.541$ Å) and $\theta$ is the Bragg's diffraction angle.

The calculated $d$-spacing of the powders (using (002) orientation plane) with various Sn contents are represented in Figure 2. This alternation in $d$-spacing may attributable to the proper replacement of smaller ionic radius of Sn$^{4+}$ (0.69 Å) at specific content on some of Zn$^{2+}$ (0.74 Å) sites leading to the noticeable spacing shrinkage in ZnO [10]. The SEM images illustrate the morphologies of as-synthesized Zn-Sn-O compound powder with different Sn content as shown in Figure 3. The SEM images disclose that the as-precipitated powders from co-precipitation process are aggregated form nanosize to microsize and has the giant cubic shape after Sn loading elevates to 60 at.%, which is corresponded to cubic phase ZnSn(OH)$_6$. 
Fig. 2. Calculated $d$-spacing of the as-synthesized compounds with difference Sn content.

Fig. 3. SEM images of as-synthesized Zn-Sn-O compounds with difference Sn content (a) pure ZnO, (b) 10 at.% Sn-loading and (c) 60 at.% Sn-loading.
4. CONCLUSION

In summary, Zn-Sn-O compound powders were successfully synthesized by co-precipitation processes. The XRD result disclosed that, without Sn loading, as-precipitated powder has a pure hexagonal wurtzite structure of ZnO. The mixed phase of ZnO and ZnSn(OH)$_6$ can be initiated after Sn loading over 30 at.% and has bare phase of ZnSn(OH)$_6$ when Sn loading over 40 at.%. It was further notified that the Sn loading has significant influence on morphological properties and phase transformation of the as-precipitated powders.

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References