In-situ Growth of Sn-Doped ZnO Nanotetrapods using Thermal CVD Method

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Abstract. Tin (Sn) insitu doping of Zinc Oxide (ZnO) nanotetrapods (T-SZnO) were successfully grown using thermal chemical vapour deposition (TCVD) method. The objective of this paper is to study the surface morphology, optical and electrical properties of the samples by varying the atomic percentage of the Sn during the deposition. All samples were annealed at temperature of 500°C for 1 hour. Field emission scanning electron microscopy (FESEM) images showed that diameter and length of nanotetrapods increased with the dopant concentration. Energy dispersive x-ray spectroscopy (EDX) showed that the nanotetrapod ZnO had been doped with Sn. Red shift was observed in the visible blue emission and a decrease in both UV and visible peaks for the photoluminescence spectra. Current-voltage (I-V) measurement showed the current increased with the dopant concentration.

1. Introduction
Wide band gap metal oxide semiconductors such as ZnO have been extensively studied since they showed great properties for many electronic devices. ZnO is a II-VI semiconductor compound with a direct band gap of $E_g = 3.37$ eV (at room temperature) [1, 2] which makes it suitable for application of shortwave length optoelectronics devices, such as light emitting diode and laser diodes. ZnO has high excitation binding energy of 60 meV, which is three times larger than GaN ($E_b = 20$ meV). Besides that, ZnO has good transparency, high electron mobility and also strong room temperature luminescence. The properties of this material depend on the deposition techniques, deposition parameter, post deposition treatment of the films and doping. The nanostructure of this material can be deposited by variety of techniques such as radio frequency (RF) sputtering, sol- gel method, thermal oxidation of metallic zinc, thermal evaporation, pulsed laser deposition (PLD) and spray pyrolysis. The nanostructure of ZnO can be found in various morphologies including nanowires, nanorods, nanotetrapods, nanobelts, nanoflowers, nanoparticle and many more. Among the various nanostructures, nanotetrapod has a unique structure which shows improved characteristics compared to others. Many devices had proven better performance when incorporated ZnO nanotetrapods, such as in gas sensors [3] and UV sensors. It also improved the polymer performance when combined into the nanocomposite thin films as fillers.

Doping is an important and effective way to improve the properties of metal-oxide semiconductors. Even though many researchers have reported on the doping of chemical vapour deposited ZnO using metal ions such as Sn [4], Ti [5], Sb [6], Mn [7] and many more which mostly focuses on the nanorods but only a few of them produced nanotetrapods.
The aim of this study is to investigate on the growth of ZnO nanotetrapods with Sn in-situ doping using thermal CVD method. The influence of different dopant concentration on surface morphology, optical properties and electrical properties of the nanostructure were characterized by FE-SEM, PL and $I-V$.

2. Experimental

2.1. Samples preparation
Glass substrates were cut with a measurement of 2.5cm x 2.5cm dimension. The glass substrates was cleaned using acetone, methanol and deionized (DI) water in ultrasonic for 10 minutes each. Then, the glass substrates were dried with nitrogen gas.

The nanotetrapod T-SZnO was synthesized using a double furnace TCVD. 2g of Zn powder ($\geq$99.9%, Sigma Aldrich) and different doping concentration of Sn was placed in two alumina boats at furnace 1 and another empty alumina boat was placed in furnace 2 for collecting the deposited sample. These boats were inserted into the quartz tube within certain diameter. Before the growth, quartz tube was put into the center area of horizontal furnace tube with the facing the direction of gas flow. Argon (Ar) which acts as the carrier gas was set at 70 sccm, while oxygen ($O_2$) gas as the reactor gas and was set at 5 sccm. The deposition temperature was set at 750 °C for furnace 1 while furnace 2 was set at 500 °C. It took 30 minutes to complete the deposition process. The white cottony product was collected once the furnace was cooled to room temperature.

The method for preparation of thin films for characterization is described as follows: A few drops of methanol solution were put into the beaker filled with the T-SZnO and stirred. A drop of solution on the substrate was rolled by a roller until the solution become uniform surface. The thin film was dried at 150°C for 10 minutes. Lastly, the nanotetrapods T-SZnO thin films were annealed at 500°C for 1 hour.

2.2. Characterization
Surface morphology and material composition of nanotetrapods T-SZnO thin film was characterized using FE-SEM and EDX (JEOL JSM-7600F). The optical properties were measured using photoluminescence emission (PL). The electrical properties T-SZnO thin films were measured using two-point probe solar simulator system (CEP 2000).

3. Result and Discussion

3.1 Surface Morphology
The surface morphology of the T-SZnO and undoped ZnO nanotetrapod was observed using field-emission scanning electron microscope (FE-SEM). The FE-SEM image was taken at 50 k magnification for 5kV, as shown in Figure 1. Figure 1 (a), (b), (c), and (d) shows the different sizes of nanotetrapods T-SZnO thin film due to different of Sn dopant concentrations. Meanwhile, Figure 1 (e) shows the size of the undoped ZnO nanotetrapods sample. It can be seen that the surface of thin films exhibit the nanotetrapod shape, where each one consists of four hexagonal rod-shaped legs connected at the center tetrahedrally. The hexagonal terminal of each leg indicates the wurtzite phase of T-SZnO crystal.

The diameter size of thin films was summarized in Table 1. The average size of the T-SZnO was found to increase with the Sn dopant concentration. The length was between 380 nm to 588 nm due to different Sn dopant concentration as shown in Table 1 as compared to the sample of undoped ZnO the length of the nanotetrapod was 330nm. Based on the result, the sizes of nanotetrapod T-SZnO was much bigger than the size of undoped ZnO. This proves that the changes in morphology of the T-SZnO nanotetrapods might due to the substantive influence of Sn-ion into the ZnO crystals.
Figure 1. FESEM images of nanotetrapod T-SZnO films at (a) 2%, (b) 4%, (c) 6%, (d) 8%, (e) undoped.

Table 1. The length and diameter of T-SZnO samples at different Sn concentrations

| Sn Concentration (at%) | Length (nm) | Diameter (nm) |
|------------------------|-------------|---------------|
| 0                      | 330         | 72.9          |
| 2                      | 380         | 110           |
| 4                      | 400         | 115           |
| 6                      | 551         | 121           |
| 8                      | 588         | 126           |

The chemical compositions of the T-SZnO thin film were measured using energy dispersive x-ray spectroscopy (EDX). The EDX spectrum of nanotetrapods T-SZnO thin film is shown in Figure 2 and it is confirmed that the nanotetrapods contains Sn which showed that the T-SZnO was successfully doped during the growth process. The EDX spectrum shows that the major compositions for T-SZnO nanotetrapod thin films are Sn (0.48 %), Zn (44.40 %) and O (50.00 %).

Figure 2. EDX spectra of nanotetrapod T-SZnO.
3.2 Optical Properties

The optical properties of nanotetrapod T-SZnO thin film were observed by photoluminescence (PL) emission at room temperature. The wavelength was taken in the range of 350 to 700 nm. Figure 3 shows the PL spectra of T-SZnO at different concentration of Sn. Based on the PL results, it is noticed that there are peaks at ultra violet (UV) emission at about 390 nm wavelength with a secondary blue peak next to it. The UV band is corresponding to the near band-edge (NBE) emission, while for visible emission is normally related to ionized oxygen vacancies and defect. Interestingly the intensity of both UV and blue emission decrease with the increase of the Sn doping. Besides that, it is clearly observed that both UV and blue emission shifted to higher wavelength side (from 406 nm for sample 2% to 420 nm for sample 8%) in addition to the decrease of intensity. This red shift of the UV emission indicates a reduction of the ZnO band gap caused by the Sn doping. The red shifting of PL was also reported by Ye et al. [8]. According to Ameen et. al [9], the Sn-ion might take part in the substitution of Zn ion which resulted in red shifting of the visible emission.

![Figure 3. PL spectra of nanotetrapod T-SZnO thin film at i) 2%, (ii) 4%, (iii) 6%, and (iv) 8%](image)

3.3 Electrical Properties

The current - voltage (I-V) measurement was measured to study the effect on the electrical properties of T-SZnO thin film. The I-V measurement of nanotetrapod T-SZnO thin film was measured using two-point probe solar simulator within voltage of -8 V to 8 V. Figure 4 shows the current-voltage of nanotetrapod T-SZnO thin films with different Sn concentrations at room temperature. The (I-V) curves are rectifying which indicates that the metal contact was reacting with the thin films.

The graph indicates that the current of T-SZnO increased with the concentration of Sn doping, which showed that the dopant improves the electrical characteristic of the thin films. We can state that the increases of dopant concentration might increase the current intensity because of increase of electron concentration and electron mobility [8]. Besides that, it might have contributed by the reduction of the thin films’ band gap.
4. Conclusion

A high quality Sn doped ZnO (T-SZnO) nanotetrapods were successfully synthesized using thermal-CVD method with different Sn concentration. The effect of Sn doping in ZnO indicates significant morphological changes whereby the FESEM results showed that there is an increased in the nanotetrapods sizes. This reveals the incorporation of Sn-ion into ZnO crystals. Similar result is also shown by the red shifting of the visible emission of the PL spectra. The I-V curve showed the current of thin film increased with the increase of the dopant concentration.

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References

[1] A. B. Djurišić, A. M. C. Ng, and X. Y. Chen, Progress in Quantum Electronics, vol. 34, pp. 191-259, 2010.
[2] I.-M. Chan and F. C. Hong, Thin Solid Films, vol. 450, pp. 304-311, 2004.
[3] M. Carotta, A. d. Cervi, V. Di Natale, S. Gherardi, A. Giberti, V. Guidi, et al Sensors and Actuators B: Chemical, vol. 137, pp. 164-169, 2009.
[4] X. Zhou, T. Lin, Y. Liu, C. Wu, X. Zeng, D. Jiang, et al., ACS applied materials & interfaces, vol. 5, pp. 10067-10073, 2013.
[5] K. Zheng, L. Gu, D. Sun, X. Mo, and G. Chen Materials Science and Engineering: B, vol. 166, pp. 104-107, 2010.
[6] Q. J. Feng, S. Liu, Y. Liu, H. F. Zhao, J. Y. Lu, K. Tang, et al., Materials Science in Semiconductor Processing, vol. 29, pp. 188-192, 2015.
[7] H. Yan, X. Zhong, J. Wang, G. Huang, S. Ding, G. Zhou, et al., Applied physics letters, vol. 90, p. 082503, 2007.
[8] N. Ye, J. Qi, Z. Qi, X. Zhang, Y. Yang, J. Liu, et al., *Journal of Power Sources*, vol. 195, pp. 5806-5809, 2010.

[9] S. Ameen, M. S. Akhtar, H.-K. Seo, Y. S. Kim, and H. S. Shin, *Chemical Engineering Journal*, vol. 187, pp. 351-356, 2012.