Structural Properties of ZnO/SnO₂-Composite-Nanorod Deposited Using Thermal Chemical Vapour Deposition

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Abstract. In this work, we report on the effect of substrate temperatures on ZnO/SnO₂ composite nanorods deposited by thermal chemical vapour deposition (CVD) onto a ZnO template layer. The substrate temperature varied from 200 ~ 600°C. The FESEM image reveals that the size of the thin film created by the ZnO/SnO₂ composite nanorods decreased as the substrate temperature increased.

1. Introduction

SnO₂ is a promising candidate for nanotechnology applications. SnO₂ is an n-type semiconductor possessing a wide band gap (3.6 eV). The electronic conductivity of SnO₂ is significantly influenced by the effects of molecular adsorption on its surface [1]. It is considered to be a good candidate sensor material because of the wide applications inherent to its defect structure and the variable oxidation state of Sn [2]. SnO₂ nanostructures can be prepared by many methods, such as chemical vapour deposition [3], radio frequency (RF) magnetron sputtering [4], the sol-gel method [5], spray-pyrolysis [6], and hydrothermally [7]. The advantageous properties of SnO₂ include good optical, chemical, electrical and thermal stabilities that enhance the abilities of this material in various device applications, such as solar cells [8], gas sensors [9] and light emitting diodes (LEDs) [10].

ZnO is naturally an n-type semiconductor material with direct band gap energy of 3.37 eV at room temperature and has a free-exciton binding energy of 60 meV [11, 12]. ZnO has been proposed for many technological applications, such as optical devices, solar cells, piezoelectric devices, varistors, surface acoustic wave (SAW) devices and gas sensors [12]. The properties of ZnO, including the electrical and optical properties, heavily depend on its crystallinity, crystallographic orientation, crystal size and morphology [12]. It has been proposed for numerous functions as a semiconductor material including as a catalyst, conduction layer and transport layer for device fabrication.

Many researchers have been exploring using composites to improve performance in many applications. ZnO/SnO₂ composites have been proposed for various applications such as OLEDs, gas...
sensors and solar cells. The advantage of these materials is their high electron mobility and improvement in surface reactions as a result of surface modification. A substrate temperature study is important in order to produce high quality of ZnO/SnO₂ composite nanorods. The issue of sensor problems such as low sensitivity and high defect are generally caused by low temperature processing during the growth phase. This is the first work that reports on ZnO/SnO₂ composite nanorods deposited using different substrate temperatures via thermal CVD methods. In this paper, we study the effect of substrate temperature on the properties of ZnO/SnO₂ composite nanorod growth when deposited using thermal CVD on a ZnO template.

2. Methodology
2.1 ZnO template preparation
The ZnO template was prepared using sputtering system. A glass substrate was used to prepare the ZnO template. The glass substrate was cleaned with acetone, methanol and deionised water via several steps before experimentation. A ZnO target (high purity (99.999%)) was used to deposit the ZnO template. The sputtering system was set at 200 watts with a pressure maintained at 7 mTorr. A molecular pump was used to evacuate the sputtering chamber to 5x10⁻⁴ Pa. Argon gas was injected into the remaining oxygen at a ratio of 45:5 sccm. The substrate temperature was set to 500°C and the deposit time was 60 min.

2.2 ZnO/SnO₂ composite nanorods preparation
The ZnO templates were used for the ZnO/SnO₂ composite nanorod deposition. Two furnaces were used to grow doped ZnO/SnO₂ composite nanorods. A quartz tube was inserted in the furnace. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%, System, Laboratory Chemicals And Reagents, Classic chemicals Sdn. Bhd.) and tin(IV) chloride pentahydrate (SnCl₄·H₂O, 98%, Sigma Aldrich) were used as the precursor and were placed inside furnace 1. The ZnO template was placed in furnace 2. The argon (Ar) and oxygen (O₂) were injected at 40 sccm and 5 sccm, respectively. The mass of both precursors was set at 3 g. The substrate temperature varied from 200 ~ 600°C over a deposition time of 1 hour.

2.3 ZnO/SnO₂ composite nanorods preparation
The surface morphology was characterised using FESEM (JEOL JSM 6701F) and the crystalline properties of the ZnO/SnO₂ composite nanorods were characterised using x-ray diffraction (XRD, Rigaku Ultima IV).

3. Results and discussions
Figure 1 shows the FESEM images of the ZnO/SnO₂ composite nanorods synthesised at different substrate temperatures: (a) 200°C, (b) 300 °C, (c) 400°C, (d) 500°C and (e) 600°C for a working voltage of 5 kV and magnifications of 30,000x and 100,000x. The insets in Figures 1 (a), (b), (c), (d) and (e) show the measured sizes of all of the samples. These surface images show that all of the thin films were uniformly deposited onto the ZnO template layer. At a substrate temperature of 200°C, the size of the nanostructures ranged from approximately 128 to 165 nm, as shown in Figures 1 (a). Figures 1(b) and (c) show the ZnO/SnO₂ composite nanorods with lengths of approximately 185 to 550 nm and 163 to 279 nm that were fabricated using substrate temperatures of 300°C and 400°C, respectively. Figures 1 (g-h) show that as the substrate temperature increases to 500°C, the ZnO/SnO₂ composite nanorods grew in alignment on the ZnO template layer with lengths of approximately 185 to 550 nm and 163 to 279 nm that were fabricated using substrate temperatures of 300°C and 400°C, respectively. Figures 1 (g-h) show that as the substrate temperature increases to 500°C, the ZnO/SnO₂ composite nanorods grew in alignment on the ZnO template layer with lengths of approximately 185 to 550 nm and 163 to 279 nm that were fabricated using substrate temperatures of 300°C and 400°C, respectively. This behaviour may have been caused by the substrate starting to melt; the melting temperature of glass is 565°C [13]. This result also shows that the ZnO/SnO₂ composite nanorods became closely packed at
high substrate temperatures. The density of the ZnO and SnO$_2$ crystal nuclei within the nucleated phase is expected to increase with the decomposition temperature. Thus, the collision frequency of the particles increases. Increasing the substrate temperature can facilitate better atomic packing and enhance the crystalline quality of the film [14, 15]. The substrate temperature influences the growth of the ZnO/SnO$_2$ composite nanorods formed by thermal CVD [16, 17]. The thickness of the ZnO/SnO$_2$ composite nanorods formed at substrate temperatures of 200, 300, 400, 500 and 600ºC were approximately 476 nm, 580 nm, 748 nm, 850 nm and 568 nm, respectively. The different morphology sizes resulted from changing the ratios of the Zn, Sn and O$_2$ vapour pressures at high temperatures [18, 19].

![Figure 1. Surface Images of the ZnO/SnO$_2$ Composite Nanorods at Different Substrate Temperatures: (a) 200ºC, (b) 300 ºC, (c) 400ºC, (d) 500ºC and (e) 600ºC.](image-url)
In our experiments, the Zn vaporised first because the Zn source had a lower melting point than the Sn source. In the evaporation process, vaporised Zn and Sn atoms impinged on the substrate and were adsorbed by the ZnO template layer. Then, the atoms reacted with the ZnO template layer and formed a bond. Two conditions arose during the growth process at low and high substrate temperatures. At low temperatures, the surface diffusion energy was insufficient to form nanorods, and the deposited atoms on the substrate had limited surface diffusion energy. This decreased the diffusion length and mobility of the atoms, thereby affecting the accumulation of the constituent atoms on the substrate [20, 21]. Atoms that were deposited at low temperatures were quenched from the high source temperature to the low temperature of the substrate. Decreasing the temperature from the evaporation temperature to the substrate temperature affected factors such as the temperature and the partial pressures, which may have affected the direction of the growth of the nanostructures [22]. At high temperatures, the crystallinity of the ZnO/SnO$_2$ composite nanorods improved due to the enhancement in the surface diffusion and the mobility of the adatoms on the substrate surface. Surface diffusion facilitated the transport of these adatoms and their nucleation into nanorod structures as the Zn particles condensed to form liquid droplets on the ZnO template layer. This nucleation form is preferred for the nanorods on the substrate with face grains [21]. Besides, the ZnO template was important to act as the holder or based for ZnO/SnO$_2$ composite nanorods. Moreover, the growth of ZnO/SnO$_2$ composite nanorods on the ZnO template was used to increase the adherent between the substrate and the ZnO/SnO$_2$ composite nanorods. In sensor application, the ZnO template can act as the transport layer to the ZnO/SnO$_2$ composite nanorods.

**Figure 2.** EDS images for ZnO/SnO$_2$ Composite Nanorods at Different Substrate Temperatures: (a) 300 °C, (b) 500°C and (c) 600°C
Figure 3. EDS spectrum images for ZnO/SnO$_2$ Composite Nanorods at Different Substrate Temperatures: (a) 200ºC, (b) 300 ºC, (c) 500ºC and (d) 600ºC.

Table 1: Atomic percent of ZnO nanoparticle, SnO$_2$ nanorod and ZnO/SnO$_2$ nanoflower like structures.

|       | Zn  | Sn  | Si  | O   | C   | Cl  |
|-------|-----|-----|-----|-----|-----|-----|
| 200ºC | 20.17 | 0 | 14.11 | 59.94 | 5.77 | 0   |
| 300ºC | 26.99 | 7.00 | 3.91 | 56.39 | 3.79 | 1.91 |
| 500ºC | 4.88 | 28.81 | 1.27 | 65.94 | 0   | 0   |
| 600ºC | 2.84 | 29.36 | 2.08 | 65.72 | 0   | 0   |

Table 1 above show the atomic percent of ZnO/SnO$_2$ composite nanorods for (a) 200ºC, (b) 300 ºC, (c) 500ºC and (d) 600ºC as refer to the EDS spectrum images in Figure 2. Table 1 and Figure 3 show the possible corresponding atomic percent(%). It reveals that the element at substrate temperature 200ºC the zinc (Zn), oxygen (O) silicon (Si) and carbon (C). As the substrate temperature increase to 300ºC, the elements consist of tin (Sn), zinc (Zn), oxygen (O) silicon (Si) and carbon (C).
Figure 4. XRD Patterns for the ZnO/SnO$_2$ Composite Nanorods at Different Substrate Temperatures: (a) 200ºC, (b) 300 ºC, (c) 400ºC, (d) 500ºC and (e) 600ºC.

Figure 4 shows the XRD patterns for the ZnO/SnO$_2$ composite nanorods at different substrate temperatures: (a) 200ºC, (b) 300 ºC, (c) 400ºC, (d) 500ºC and (e) 600ºC. The XRD patterns of these samples at different substrate temperatures exhibited diffraction peaks corresponding to hexagonal wurzite ZnO (JCPDS card no. 36-1451). The diffraction peaks for ZnO that were formed at a substrate temperature of 200ºC appeared at (100), (002), (101), (102), (110), (103) and (112). All of the diffraction peaks could be perfectly indexed to the hexagonal wuritzite structure of ZnO and the tetragonal anatase-rutile crystal of SnO$_2$ (JCPDS card no. 41-1445), as shown in Figure 4 (b) for substrate temperatures of 300 ºC, (c) 400ºC, (d) 500ºC and (e) 600ºC. For the diffraction peaks obtained for samples that were synthesised at substrate temperatures of 300 ºC, the major peaks corresponded to the hexagonal wurzite structure of ZnO and were indexed to (100), (002), (101), (102), (110), (103) and (112), whereas the minor peaks were assigned to SnO$_2$ and were indexed to (110) and (111). For the substrate temperatures of 400ºC, 500ºC and 600ºC, minor ZnO peaks appeared at (110). However, the peaks for the SnO$_2$ phase were assigned to (110), (101), (211), (002) and (301). The reaction of the ZnO and SnO$_2$ began at a substrate temperature of 300ºC, as shown in Figure 4 (b), with the formation of the SnO$_2$ orientation first. The crystallinity of the ZnO/SnO$_2$ composite nanorods improved because of the high deposition rate at the high substrate temperatures, which increased the electron mobility in the composite nanorods [20]. The enhanced crystallinity improved the performance of a sensor application. As the substrate temperature increased from 400ºC to 600ºC, a small amount of the ZnO phase with a peak at (100) was formed, and the amount of the SnO$_2$ phase increased. Al-Ghaashi et al. [18] studied the thermal decomposition of tin (II) chloride dehydrate at different substrate temperatures (over a range of 300 to 900 ºC) and found that the growth of SnO$_2$ crystal nuclei began at approximately 400ºC. This result supports the XRD results shown in
Figure 4, where the SnO\textsubscript{2} major crystal structure formation begins at 400\degree C. The SnO\textsubscript{2} phase with a preferential (101) orientation exhibited the highest intensity because of its low surface energy [23, 24].

4. Conclusions

In summary, ZnO/SnO\textsubscript{2} composite nanorods were successfully prepared on a ZnO template using thermal CVD. The size of ZnO/SnO\textsubscript{2} composite nanorods decreased as the substrate temperature increased. Zinc nitrate and tin tetrachloride were used as precursors. Observation of the initial growth phase of ZnO crystal began to form at 200 \degree C and for SnO\textsubscript{2} crystal nuclei began to form at approximately 300 \degree C. Enhancing the crystallinity of the ZnO/SnO\textsubscript{2} composite nanorods improved the sensing characteristics.

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6. References

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