

The influence of Sn doping on the structural and morphology of ZnO nanowire deposited using PVD technique

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The thin film of ZnO nanowire and Sn-doped ZnO nanobelt were fabricated through physical vapor deposition (PVD) technique on Si (111) substrate. X-ray Diffraction (XRD) and Energy Dispersive X-ray (EDX) studies demonstrated that there are significant change in crystal structure and content of the elements as the nano structures change from nanowire to nanobelt when the ZnO thin film was doped with Sn. The morphological change in the shape of the nanostructure from nanowire to nanobelt and to nanoring can be observed from the Field Effect Scanning Electron Microscopy (FESEM) images. The high polarity of Sn-doped ZnO has caused the formation of the spiral structure in the nanostructure of the ZnO thin film.

I. INTRODUCTION

Zinc oxide is a semiconductor with hexagonal wurtzite crystal structure. Its lattice constants, a , is between 0.324 nm and 0.326 nm and c is between 0.513 nm and 0.543 nm. Wurtzite is the most common and stable crystal structure in ambient condition [1]. ZnO has wide and direct band gap which is nearly 3.37 eV at room temperature and visible light transparent. It is also a reliable room temperature and high temperature luminescence material as it has a large exciton binding energy which is about 60 meV [2,3]. Zinc oxide is widely used as semi conducting material. It is applicable as electronic and optoelectronic device material such as transparent conductor, gas sensor, solar cell and display window due to their n-type conducting property with optical transparency in the visible range [4,5]. ZnO is also used in sensor and actuator because as it also exhibits piezoelectric (especially for high frequency) and pyroelectric properties. Some ZnO also has been reported to be used in biomedical science as it is biocompatible, biodegradable and non-toxic [2].

Nowadays doped ZnO thin film has been numerously studied for their use as transparent conducting electrode material [6]. This non-toxic transparent material becomes conductive when it is doped [7]. Elements that can be selected as dopant are classified into two groups of material. One group of material is used to substitute Zn while the other group is used to substitute O [8]. Sn-doping as cation can be used to substitute Zn and it has been reported that it can induced an emission at blue wavelength region [9,10].

In this work, pure zinc oxide and Sn-doped zinc oxide have been prepared using physical vapour deposition (PVD) method on silicon substrate. The differences in the physical and optical properties, such as the morphology and photoluminescence for both

nanostructure materials, were investigated. The morphology of the samples was characterized using (XRD) and (FESEM). (EDX) was used to observe the contents of the elements in the sample.

II. EXPERIMENTAL

The nanowire and nanobelt ZnO thin films were deposited on Si (111) substrate via physical vapor deposition technique (PVD) using calibrated horizontal furnace. Powder form of ZnO, graphite and tin oxide (SnO) were used as deposition source. The deposition source for nanowire ZnO and nanobelt ZnO with Sn-doped were prepared by mixing the ZnO:graphite:SnO with the weight ratio of 1:1:0 and 1:1:0.5, respectively. Initially, the Si substrates were cleaned by following steps; the substrates were immersed in hydrochloric acid (HCl) aqueous, rinsed with distilled water, immersed in sodium hydroxide (NaOH), and rinsed with distilled water again. Then the substrates were immersed in HF solution and rinsed with distilled water in order to create holes on substrate surface. Finally, the substrates were purged by nitrogen gas for drying purposes. The deposition source was placed at center position inside the calibrated furnace to achieve maximum temperature. The cleaned Si substrates were placed next to the deposition source. The pressure of the furnace tube was maintained around 13.3 torr. The N₂ gas which acts as carrier gas was passed through the furnace tube with a flow rate of 50 sccm. The source and substrate were heated up to the temperature of 950 and 500°C, respectively during the deposition process. Both nanostructured ZnO thin films were deposited for about an hour. Fig. 1 shows the schematic diagram of the setup used for the deposition process in this work.

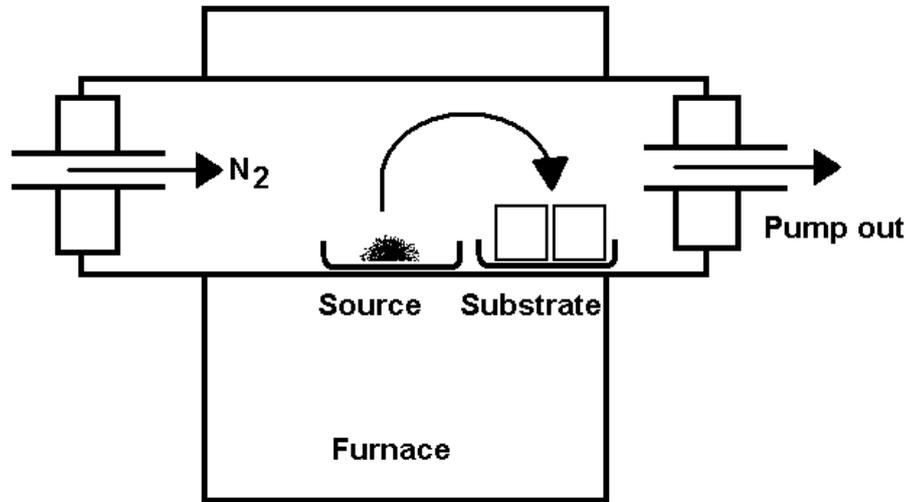


FIG. 1. The schematic diagram of the setup of the physical vapor deposition system.

The morphology and crystal nanostructure of the samples were analyzed using X-ray Diffraction (XRD, Siemens D5000) and Field Emission Scanning Electron Microscopy (FESEM, FEIPUANTA 200 SESC), respectively. The element contents of the samples were determined by using Energy Dispersive X-ray (EDX, FEIPUANTA 200 SESC). The thickness of the crystal nanostructure thin films was measured by a surface profiler meter (KLA TENCOR P-16+/P-6).

III. RESULTS AND DISCUSSION

IIIa. XRD Pattern

The crystallinity of the samples was studied by XRD measurement in room temperature. Fig. 2 shows the XRD patterns of the nanostructured thin films of ZnO and Sn-doped ZnO growth on Si (111) substrate. For the pure ZnO, the preferred orientation of the ZnO nanowires at high temperature zones was obtained at plane (002), therefore ZnO nanowires show the c-axis preferred orientation, namely along [001]. The highest peak of Zn₂SnO₄ thin film was located at plane (311). The plane (311) is therefore suitable for the formation of the Sn-doped ZnO nanobelts. By using the Bragg's law equation;

$$2d \sin \theta = n\lambda \tag{1}$$

where λ is the wavelength of the incoming x-ray radiation and it is equal to 1.5406 Å, d is lattice distance of the crystal planes, n is the order of the diffraction when $n = 1$ is used, θ is the diffraction angle. From Equation (1), the lattice distance value, d can be calculated. The value of the lattice mismatch can be directly calculated using the formula below:

$$\frac{d_{Si(111)} - d_{(ZnO)}}{d_{Si(111)}} \times 100\% \tag{2}$$

In Equation (2), $d_{Si(111)}$ and $d_{(ZnO)}$ are the lattice distances of the Si(111) substrate and the nanostructure ZnO, respectively. The values of the lattice parameters were presented in Table I. The large lattice mismatch in both samples was believed due to the high chamber pressure used and it has been reported that the ideal chamber pressure for good alignment quality must less than 1.5 mbar [11].

TABLE I. The values of the lattice parameters.

	Lattice distance d (Å)	Lattice mismatch Δd (%)
ZnO	2.81	50.9
Zn ₂ SnO ₄	2.61	52.0

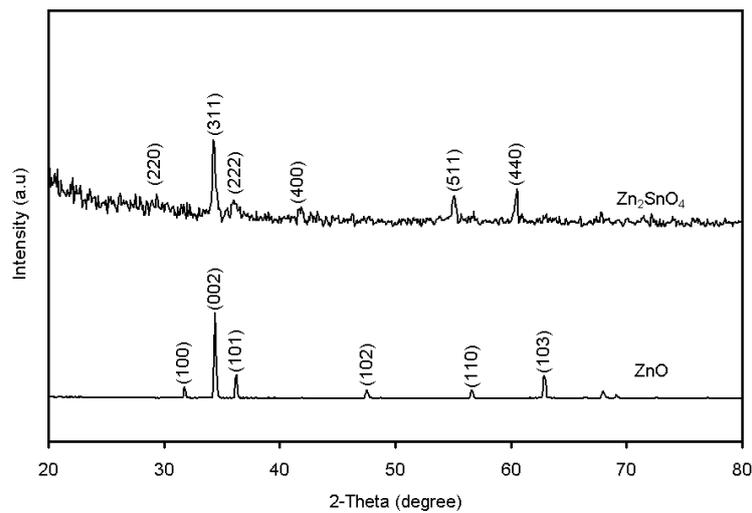


FIG. 2. The XRD pattern of the nanostructure thin films of ZnO and Sn-doped ZnO.

IIIb. EDX Result

The contents of the corresponding elements of the nanostructure samples were study by EDX. Fig. 3 shows the EDX spectra of the nanostructure thin films of ZnO and Sn-doped ZnO. The elements of the ZnO nanoparticles were detected as reported by Ramin *et al.* [8]. It indicates the formation of pure ZnO thin film. The atomic percentage of oxide (O) and Zn are 42.45 and 57.55%, respectively. The EDX spectrum of the Zn₂SnO₄ thin film indicates the presence of Sn and Si elements in the nanobelt sample. The atomic percentage of Sn obtained is about 1.58%, while the atomic contents of O and Zn are about 36.31% and 9.12%, respectively. The highest peak in the spectrum corresponds to Si element with atomic percentage of 53%. It is most probably due to some part of the surface of the Si substrate surface was not covered by the nanostructure thin films during the deposition process. The percentages of the elements in the nanostructure thin films are shown in Table II.

TABLE II. The elements of the nanostructure thin films.

	Atomic contents (%)		
	Zn	O	Sn
ZnO	57.55	42.45	-
Zn ₂ SnO ₄	9.12	36.31	1.58

IIIc. FESEM Image

Fig. 4 and Fig. 5 show the FESEM images of the nanowire ZnO and the nanobelt Sn-doped ZnO, respectively. The nano wire ZnO growth in random direction with various shapes and sizes. However, most of the nano wire grow with the hexagonal shape which is aligned with the XRD results as shown in Fig. 3. At higher magnification, the measured diameter of the nano wire is around 100 to 350 nm. In Fig. 5, some parts of the nanobelts have formed inversed spinel of Zn₂SnO₄ phase (marked as yellow box) which is very dense belt-like nanostructure [12]. Doping Sn atom into ZnO has affected the groth process of ZnO. The structure becomes complex and forms nanobelt. As a result of polarity in the doped ZnO nanobelt, the structure of the nanobelt change to nanoring[13]. The diameter and shape of the nanobelt were significantly smaller than that of the nanowire structure shown in Fig. 4. The diameter of the doped nanostructure is obtained around 30 to 35 nm. The different in the morphology of the ZnO as it grow originated from the ZnO itself, where they have several unique nanostructures like nanowire and nanobelt which have different quasi-stable surface and corresponding growth direction [2]. The presence of Sn atom is believed to have created different surface charges at several parts of the nanobelt ZnO. During the growth, these polar-nanobelt surfaces may tend to fold themselves to minimize the area of surface polar. The length of the other polarity is getting longer as illustrated in Fig. 6.

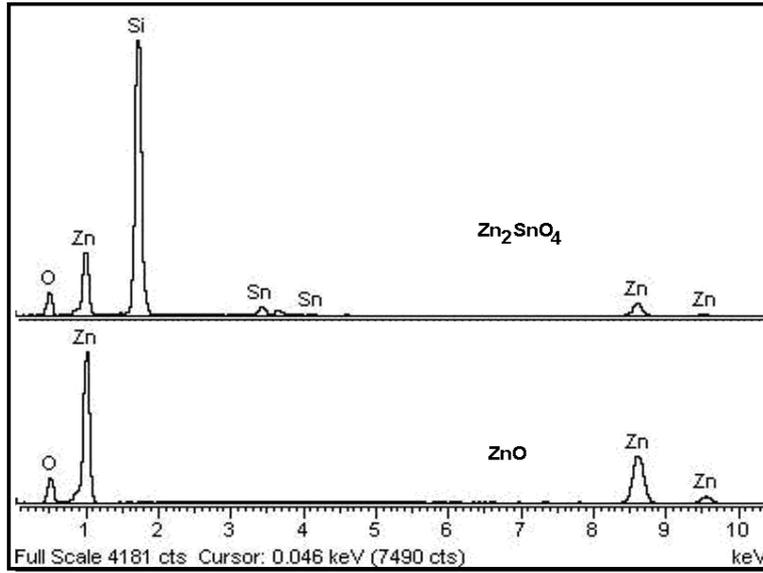


FIG. 3. The EDX spectra of the nanostructure thin films of ZnO and Sn-doped ZnO.

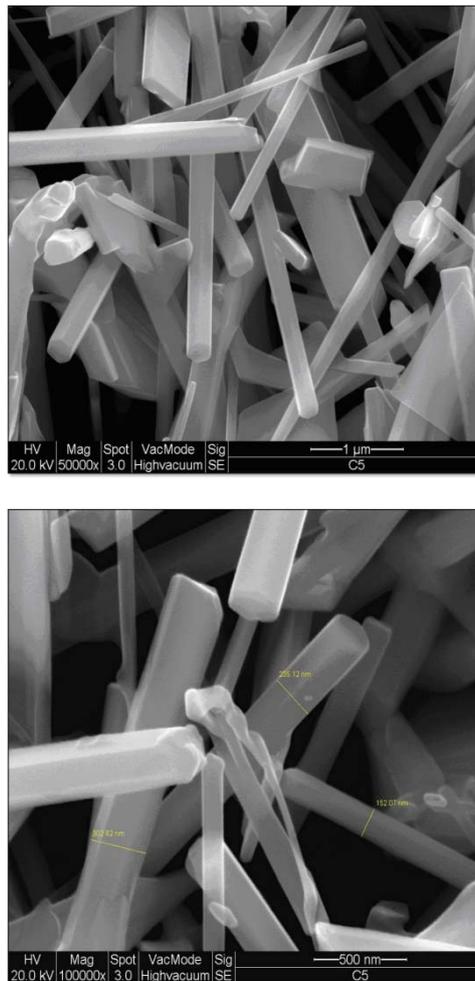


FIG. 4. The FESEM micrographs of the nanowire ZnO at different magnifications.

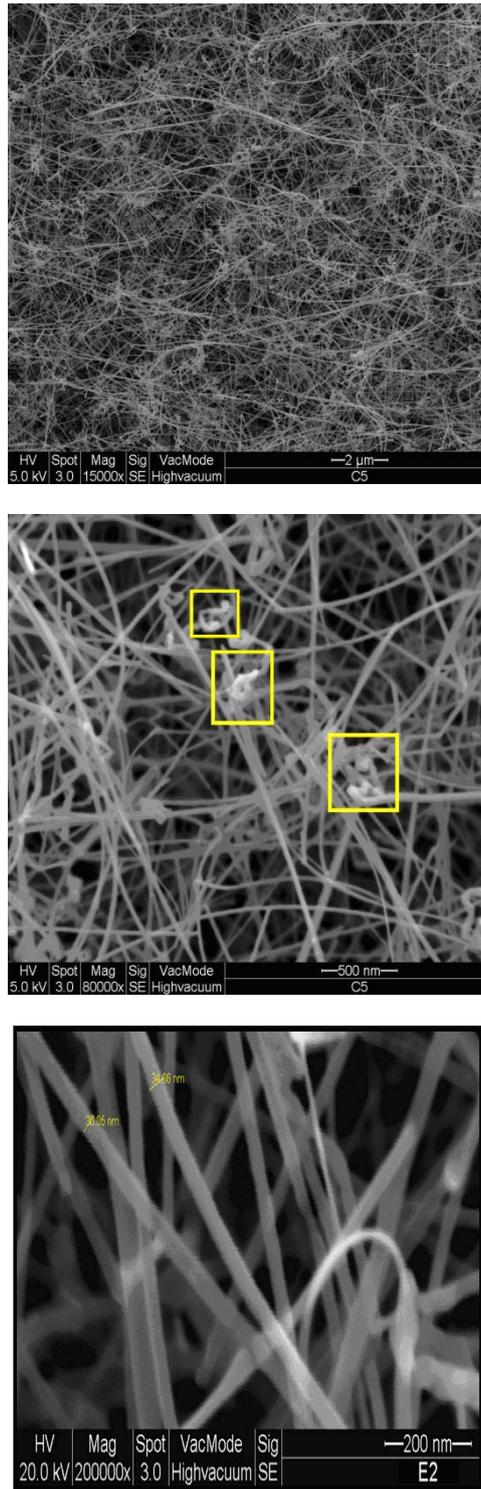


FIG. 5. The FESEM micrographs of the nanobelt ZnO at different magnifications.

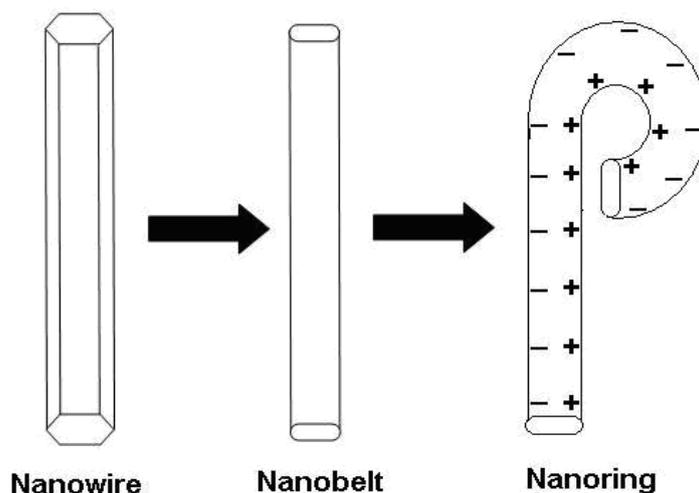


FIG. 6. The proposed change in the nanostructure of the ZnO thin films during growing process.

IV. CONCLUSION

In summary, the nanowire and nanobelt ZnO can be fabricated using physical vapor deposition (PVD) technique using fixed deposition parameters. The XRD results showed that both nanostructure films have large lattice mismatch which is mainly attributed to the high chamber pressure used in the deposition process. Doping ZnO with Sn atom can change the nanostructure of the ZnO from nanowire to nanobelt. Sn atom also plays an important role to enhance the polarity of several parts of ZnO nanobelt which creates the spiral structure that resembles the nanoring structure. Thus, Sn atom is a suitable dopant for low deposition pressure in PVD technique to change ZnO nanowire into nanobelt, and also to grow the nanoring.

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REFERENCE

[1] Yunhua Huang, Yue Zhang, Jian He, Ying Dai, Yousong Gu, Zhen Ji and Cheng Zhou, *Ceram. Int.*, **32**, 561-566 (2006).

[2] Zhong Lin Wang, *Materials Science and Engineering*, **64**, 33-71 (2009).

[3] O. Lupan, V. M. Guérin, I. M. Tiginyanu, V. V. Ursaki, L. Chow, H. Heinrich and T. Pauporté, *Journal of Photochemistry and Photobiology A: Chemistry*, **211**, 65-73 (2010).

[4] Y. Natsume, H. Sakata, *Thin Solid Films*, **372**, 30-36 (2000).

[5] L. Miao, Y. Ieda, S. Tanemura, Y. G. Cao, M. Tanemura, Y. Hayashi, S. Toh and K. Kaneko, *Sci. Technol. Adv. Mat.*, **8**, 443-447 (2007).

[6] H. Kim, A. Piqué, J. S. Horwitz, H. Murata, Z. H. Kafafi, C. M. Gilmore and D. B. Chrisey, *Thin Solid Films*, **377**, 798-802 (2000).

[7] Z. Ben Achour, T. Ktari, B. Ouertani, O. Touayar, B. Bessais and J. Ben Brahim, *Sensors and Actuators A: Physical*, **134**, 447-451 (2007).

[8] Ramin Yousefi and Burhanuddin Kamaluddin, *Appl. Surf. Sci.*, **255**, 9376-9380 (2009).

[9] S. Y. Bae, H. W. Seo, D. S. Han, M. S. Park, W. S. Jang, C. W. Na, J. Park and C. S. Park, *J. Cryst. Growth*, **258**, 296-301 (2003).

[10] Yong Su, Ling Li, Yiqing Chen, Qingtao Zhou, Mi Gao, Qiong Chen and Yi Feng, *J. Cryst. Growth*, **311**, 2466-2469 (2009).

[11] Jinhui Song, Xudong Wang, Elisa Riedo and Z. L. Wang, *J. Phys. Chem. B*, **109**, 9869-9872 (2005).

[12] R. Deng, X. T. Zhang and J. Lumin., **128**, 1442-1446 (2008).

[13] X. Y. Kong, Y. Ding, R. S. Yang and Z. L. Wang, *Science*, **303**, 1348-1351 (2004).