Chiang Mai J. Sci. 2011; 38(1) : 39-46
www.science.cmu.ac.th/journal-science/josci.html
Contributed Paper

Zinc Oxide Whiskers by Thermal Oxidation Method

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Recieved: 25 March 2010
Accepted: 20 September 2010

ABSTRACT

ZnO whiskers were grown in quartz tube by thermal oxidation method. Zinc powder was heated in a horizontal quartz tube with a furnace at a temperature of 700°C for 2 hr, under normal atmosphere. Three different kinds of the products can be obtained after the oxidation process. One is transparent whiskers located at the bottom of the quartz tube. Next is cotton-like bulk and the other is white, fluffy product. The products were characterized by field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS). It was found that the products composed of whiskers and tetrapod whiskers. The lengths and the diameter of whiskers were in the range of 10-240 mm and 0.20 - 4.60 mm, respectively while the percent of yield was up to 20% by weight. The lengths and the diameter of tetrapod whiskers were in the range of 3.15-10.63 mm and 0.13- 2.64 mm while the percent of yield was up to 68% by weight.

Keywords: zinc oxide, whisker, tetrapod, thermal oxidation.

1. INTRODUCTION

Recently, quasi one-dimensional (1D) nanostructures such as whiskers, wires, rods, belts, and tubes have received the great interest due to their very large surface-to-volume ratio and become the focus of intensive research owing to their unique applications in mesoscopic physics, fabrication of nanoscale optic and electronic devices [1]. ZnO is now receiving special attention for it potential applications in optical and electronic materials [2]. It is an n-type semiconductor with a direct band gap of 3.37 eV at room temperature close in properties to GaN (E_g = 3.5 eV at room temperature), which is widely used in the fabrication of blue light emitting diodes. The strong exciton binding energy of 60 meV, which is much larger than that of GaN (25 meV) and the thermal energy at room temperature (26 meV) can ensure an efficient exciton emission at room temperature under low excitation energy [2-5]. ZnO can be grown into a variety of micro and nanostructures, such as tetrapod-shape, microrods, one-dimensional microtubes, thin film, nanobelts, nanowires, nanoneedles, nanotubes, nanorods, nanocables and whiskers [1, 6-14]. ZnO nanostuctures are particularly adaptable and have various potential applications, such as gas sensors [15, 16], solar cells [17], field emitters [18] and the field effect transistor (FET) [19]. Among them, ZnO whisker has attended due to ease of preparation and single crystalline properties.

ZnO whiskers have a hexagonal columnar shape (pencil-like structure) and ZnO whiskers, having tatrapod shape, consist of a ZnO core in the zinc blended structure form in which four ZnO arms in the wurtzite structure radiate. Each arm is well faceted with a hexagonal cross-section and is uniform in length and diameter [20]. Among kinds of ZnO whiskers, tetrapod whisker possesses good comprehensive properties, such as semiconductivity, wear resistance, vibration insulation and microwave absorption. Owing to the unusual geometry and single crystalline character, they can be widely applied as both devices and structural materials [21,22]. In particular, the introduction of ZnO tetapod whiskers imparts antielectrostatic and antibacterial properties to polyacrylate-based composites. Tetrapod-polymer composites can be used in the fabrication of solar cells. Moreover, similarly other structures, ZnO whiskers have attractive gas-sensing and luminescent properties [2].

Due to these promising applications, ZnO whiskers can be prepared by several methods such as solvothermal [1], thermal evaporation [23], Metal Organic Chemical Vapor Deposition (MOCVD) [24], Pulsed Laser Deposition (PLD) [25] and thermal oxidation [15,16,21,22]. The thermal oxidation method is a simple, low cost and fast process. So in this work, ZnO whiskers were prepared with high yield by thermal oxidation of Zn powder.

2. MATERIALS AND METHODS

ZnO whiskers were prepared by thermal oxidation technique. In typical preparation processes, Zn powder mass (Ajax Finechem, quoted purity of 99.9%) was used at weight of 3, 3.5, 4, 4.5, 5, 5.5 and 6 g then the powder was hand-grounded in agate mortar. After that, ZnO powder was put into the horizontal one-end sealed quartz tube (150 ml) to serve as the source materials. The quartz tube was then pushed into the central of a conventional tube furnace under normal atmosphere at 700°C. The gate of the furnace was closed without special sealing during the whisker generation process. After 2 hr. sintering, the quartz tube was taken out from the furnace into air for rapid cooling.

The obtained products were investigated by field emission scanning electron microscope for morphology and energy dispersive spectroscopy for chemical composition.

3. RESULTS AND DISCUSSION

Before heating, a typical color of zinc powder is grey. After heating process, Zn was oxidized with O_2 in normal atmosphere and transform to ZnO. It was observed that wall of the quartz tubes were covered with a white layer product and there were three different kinds of the products ranging from the bottom to the edge of the quartz tube. One is transparent columned whiskers located at the bottom of the quartz tube. Next is white, cotton-like bulk and other is white, fluffy product. It can be further classified in three portions according to morphologies and density, namely the first portion, the second portion and the third portion as showed in Figure 1.

The different morphologies of products in different portions due to the growth mechanism of the wire-like nanostructures including nanowires, nanorods, nanobelts and whiskers can be explained by the kinetics of anisotropic growth via a vapor-solid mechanism represented as:

$$P = B\exp\left(\frac{-\pi\sigma^2}{k_B^2 T^2 \ln(\alpha)}\right)$$

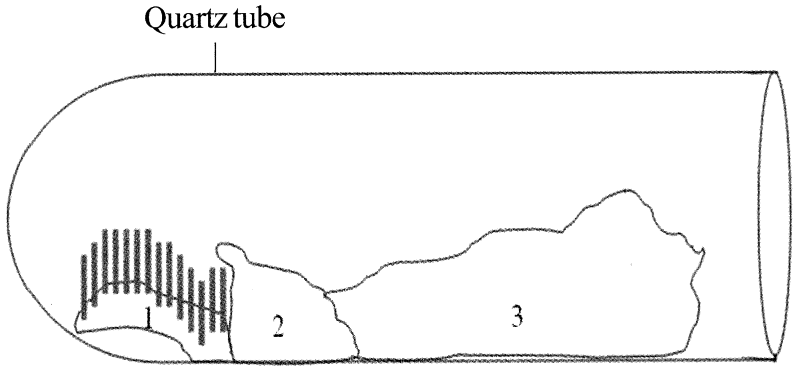


Figure 1. Schematic of the ZnO whiskers formed in different portion in the quartz tube.

where P is the nucleation probability on the surface of a whisker, B is a constant parameter, σ is the surface energy of the solid whisker, k_B is the Boltzmann's constant, T is the absolute temperature, and α is the supersaturation ratio between the actual vapor pressure and the equilibrium vapor pressure corresponding to temperature (usually, > 1) [26-28]. The supersaturation ratio play an important parameter in controlling morphology of wire-like and belt-like nanostructures[26]. Smaller supersaturation ratio promotes the growth of wire-like structures. In contrast, larger supersaturation ratio promotes two dimensional growths resulting in the formation of belt-like structures. However, the tetrapod whisker was not grown on substrate and the supersaturation ratio should be larger than belt-like structures for facilitate the three dimension nucleation resulting in the formation of tetrapod whiskers [28].

In this work Zn in gas phase can be occurred when we heat Zn metal at 700°C which above melting point of it. The mechanism can be explained based on the thermal oxidation reaction which expressed as:

$$2Zn_{(g)} + O_{2(g)} \rightarrow ZnO_{(s)}$$

The O_2 for this reaction come from the residual O_2 inside the tube at the beginning and the O_2 which enter into the quartz tube from the opened end. Then the O_2 concentration near the opened end of the tube is higher than the O_2 concentration far inside the tube therefore the supersaturation ratio of ZnO vapor near the opened end is larger than at the bottom. In this result the shape of products depend on the supersaturation ratio of ZnO vapor's zone in the quartz tube as can see from the SEM images in Figure 2 which the first portion is composed of ZnO whiskers with the hexagonal column (pencil-like structure). The diameter and length were in the range of 30-140 mm and 0.38-4.59 mm, respectively (Figure 2a). The second portion is white and quite dense. It consists of tetrapod whiskers which have the hexagonal cylinder legs. The leg-length of 7.34 ± 0.87 (6.17-9.21) μm and the diameter of 0.32-0.66 (0.49 ± 0.09) μm (Figure 2b). We obtained two types of tetrapod whiskers in the third portion. In this portion, there is the highest concentration of O_2 lead to high probability of Zn vapor oxidized with O_2. Large supersaturation ratio promotes tetrapod growth easily. The obtained tetrapod whiskers have 2 different kinds due to the growthing time. That mean tetrapod whisker in the inner layer have been grown first and the growth is continuously. Thus, the tetrapod whiskers in the inner layer will be longer and bigger than that in the outer layer as showed in the figure that the outer layer is white, fluffy which quite porous with a thickness of about 1-3 mm and it is composed of tetrapod whiskers which have the leg-length of 4.77 ± 1.46 (3.15-8.87) μm and the diameter of 0.66 ± 0.14 (0.43-0.97) μm at the base, 0.21 ± 0.05 (0.13-0.28) μm at the needle (Figure 2c). The inner layer composed of tetrapod whiskers which have the hexagonal cylinder legs. The leg-length of 7.21 ± 1.64 (4.26-10.63) μm and the diameter of 1.50 ± 0.65 (0.67-2.64) μm (Figure 2d). By SEM observation, the tetrapod whiskers become shorter in leg-length and smaller in aspect ratio as from outside to inside.

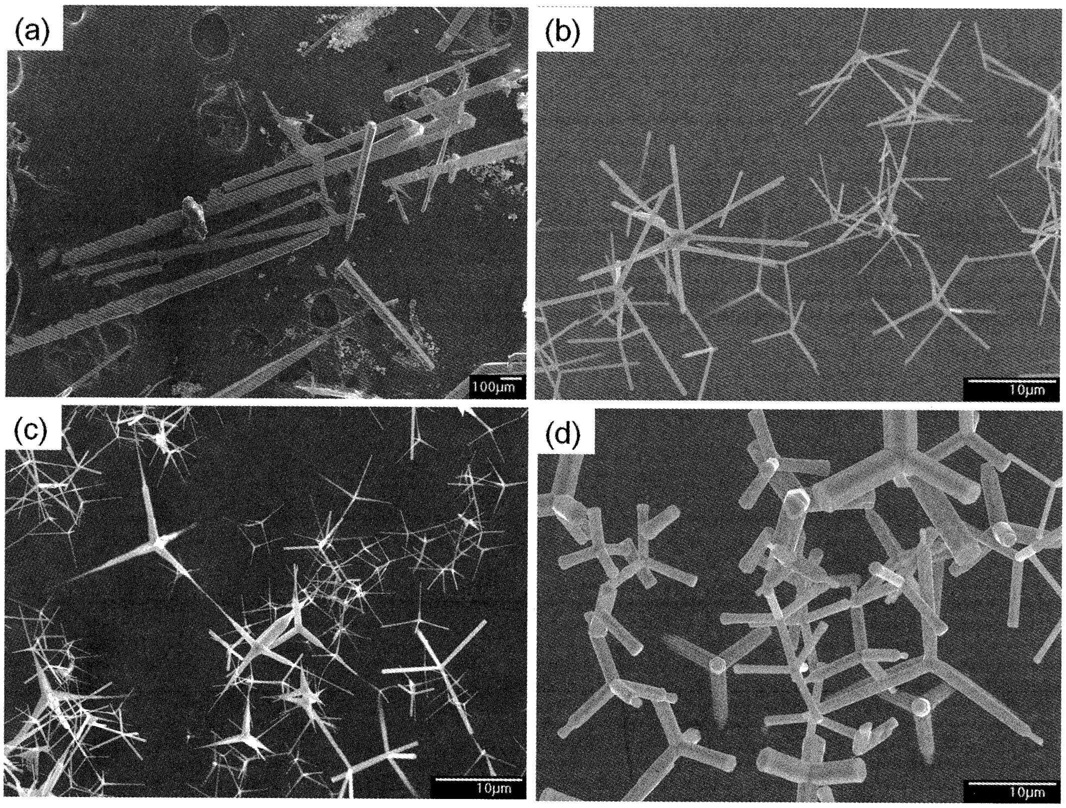
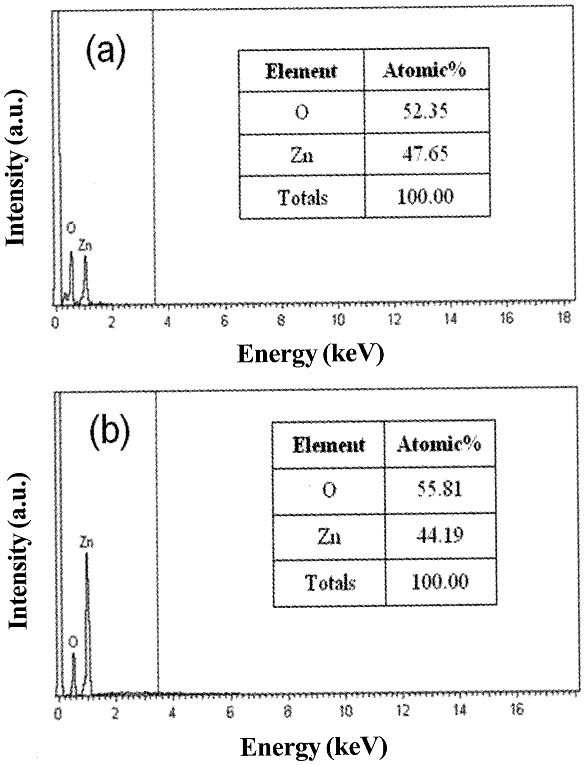


Figure 2. SEM images of ZnO whiskers in difference portions. (a) first portion, (b) second portion, (c) outer layer of third portion, d) inner layer of third portion.

Figure 3 showed EDS spectra of (a) whisker and (b) tetrapod whisker. The spectra were obtained by focusing electron beam in the top of whisker. The peaks at Zn and O signals indicated that Zn was oxidized with O and form ZnO whiskers. The atomic ratio of Zn and O from the EDS spectra of whisker and tetrapod whisker were 47.65 : 52.35 and 44.19 : 55.81, which was nearly 1:1 ratio. Thus, the obtained whisker could be considered as ZnO.

Figure 4 showed the effect of Zn powder weight on the producting yield. Producting yields of tetrapod whisker was high when the weights of Zn powder was used more than 3.5 g and it seem to be saturated. Producting yield of whiskers did not have a significant change with the change of Zn powder weight used. The obtained whiskers which prepared by thermal oxidation of Zn powder were almost hexagonal column shaped but the higher of weight of



Element	Atomic%
O	52.35
Zn	47.65
Totals	100.00

Element	Atomic%
O	55.81
Zn	44.19
Totals	100.00

Figure 3. The EDS analysis of (a) whiskers, (b) tetrapod whiskers.

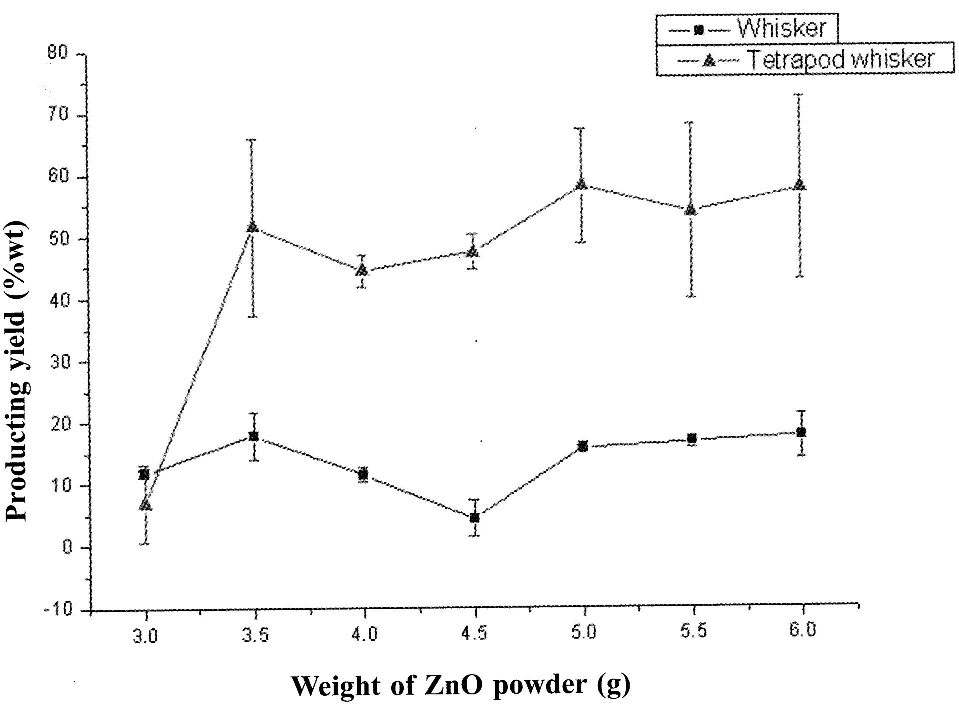


Figure 4. The effect of ZnO powder weight on the producting yield.

Zn powder led to less uniform of structure, as showed in Figure 5. Because of the high vapor pressure of Zn in the growth area, it was found that a lot of fine particles were deposited on the surface of whiskers.

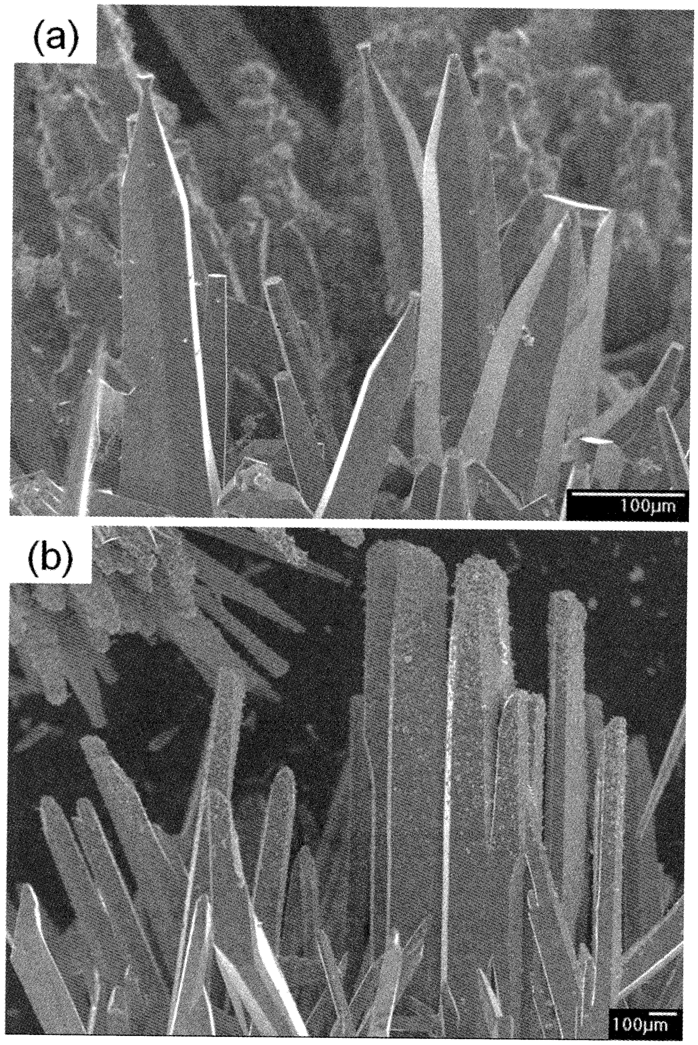


Figure 5. SEM images of ZnO whiskers which different ZnO powder weight used. (a) Zn powder 3.5 g, (b) Zn powder 5 g.

4. Conclusions

ZnO whiskers were successfully prepared by thermal oxidation method. From FE-SEM, the lengths of whiskers were in the range of 10-240 μm, the diameters were in the range of 0.20 - 4.60 μm while the percent of yield was up to 20% by weight. The lengths of tetrapod whiskers were in the range of 3.15-10.63 μm, the diameters were in the range of 0.13- 2.64 μm while the percent of yield was up to 68% by weight. From EDS, it was suggested that the chemical component is ZnO. It was found that the higher of weight Zn powder led to less uniform of structure.

ACKNOWLEDGEMENTS

This work was partially supported Thailand Research Fund (TRF). Kiattipoom Kongjai would like to acknowledge the financial support via the Graduate school, Chiang Mai University.

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