Catalyst-Free Synthesis of Zinc Oxide Nanowires by Thermal Oxidation of Zinc Film

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Zinc oxide (ZnO) nanowires with high aspect ratio were successfully synthesized by annealing the Zn films in the air prepared by electron beam evaporation. The diameter and the length of nanowires are 500 - 100 nm and 5 - 10 μm, respectively. Transmission electron microscopy analysis showed that ZnO nanowire is highly crystalline in nature. The experimental results were explained by vapor-solid growth model.

Key words: zinc oxide, nanowire, thermal oxidation

1. INTRODUCTION
Zinc oxide (ZnO) nanowires have attracted attentions for various applications, such as solar cells, photo catalyst, sensors, field emitters, etc. Although the synthesis of ZnO nanowire is relatively easy, the synthesis of uniform ZnO nanowire with high aspect ratio without using any sophisticated equipment has not been established yet.

ZnO nanowires are usually synthesized by chemical vapor deposition [1], spray pyrolysis deposition [2], sol-gel method [3], electrochemical deposition [4], hydrothermal method [5], etc. In most cases, metallic catalysts are used for the synthesis. But if it is possible to synthesize ZnO nanowires free from metals, it becomes possible to produce high-purity nanowires without containing any impurity element, resulting in the improvement of device properties.

Recently, catalyst-free synthesis has been studied by using ZnO powder, Zn powder, Zn substrate. Dai et al reported the synthesis of tetrapot-like ZnO nanorod, through the oxidation of Zn powder [6]. Sekar et al reported the synthesis of ZnO nanowire on Si substrate by the oxidation of Zn powder [7]. More recently, Ren et al reported the synthesis of ZnO nanowires by thermal oxidation of Zn substrate [8].

In this letter, we report that ZnO nanowires are synthesized by the oxidation of Zn films on glasses by electron beam (e-beam) evaporation in the air. It is shown that the ZnO nanowires with the diameter of 50 – 100 nm and the length of 5 – 10 μm are synthesized by the simple method.

2. EXPERIMENTAL
The Zn film was prepared on glass substrate using Zn wire (99.9%) by e-beam evaporation at room temperature. The thickness of Zn film is about 500 nm. The ZnO film was prepared on glass substrate by e-beam evaporation using ZnO tablet for comparison. The Zn film and ZnO film on glass substrates were heated up to 600 °C for 3 hours in the quartz tube with electric furnace. The diameter of quartz tube is 75 mm and the flow rate of dry air is 0.5 l/min. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

3. RESULTS AND DISCUSSION
Fig. 1(a) and 1(b) show the SEM images of 500 nm-thick as-deposited Zn and ZnO films prepared on glass substrate by e-beam evaporation at room temperature, respectively. In Fig. 1(a), the grain of metallic Zn with the diameter of around 400 – 500 nm are randomly observed. On the other hand, ZnO film deposited by e-beam is relatively smooth compared with Zn film as shown in Fig. 1 (b).

The SEM images of Zn and ZnO films after annealing at 600 °C are shown in Fig. 2(a) and Fig. 2(b), respectively. Fig. 2(a) reveals that high density of wire-like structures with the length of 5-10 μm are observed. On the other hand, wire-like structures are not observed in Fig. 2 (b). It means that wire-like structures are observed after annealing the Zn film in the air. On the other hand, the grain size is increased by the annealing of ZnO film, without forming wire-like structures. The cross-sectional SEM image shows that the nanowires grow towards random orientation.

In order to evaluate the crystal structure of the films, XRD measurement was performed in both samples. Fig. 3 (a) and 3 (b) show the XRD patterns taken from the Zn and ZnO films after annealing at 600 °C, respectively. All the peak in Fig. 3(a) and 3 (b) are indexed as wurtzite ZnO with lattice constant of a = b = 0.325 nm and c = 0.521 nm. No peak corresponding to Zn or other compounds are observed. It means that not only the films but also wire-like structures are ZnO.
The difference of Fig. 3 (a) and 3 (b) is due to that of crystallization process of ZnO.  

![Image](image1.png)  

**Fig. 1** SEM images of 500nm-thick Zn (a) and ZnO (b) films without annealing.

![Image](image2.png)  

**Fig. 2** SEM images of the samples with annealing Zn film (a) and ZnO film (b) at 600 °C in the air.

The ZnO nanowires were analyzed by TEM for the further investigation. Fig. 4 (a) and 4 (b) show the TEM photograph and selected-area diffraction pattern of ZnO nanowires synthesized by annealing Zn film at 600 °C for 3 hours in the air, respectively. The diameter of ZnO nanowire is determined to be around 80 nm and the ZnO nanowire is single crystalline with hexagonal structure. It means that the single crystalline ZnO nanowires are synthesized by annealing the Zn films deposited by e-beam evaporation in the air. The TEM observation of several ZnO nanowires indicates that the diameter is between 50 – 100 nm.

![Image](image3.png)  

**Fig. 3** XRD pattern of ZnO films with annealing Zn film (a) and ZnO film (b) at 600 °C in the air.

The vapor-liquid-solid (VLS) mechanism and vapor-solid (VS) mechanism have been proposed for the growth of ZnO nanowires [9, 10]. But our results cannot be explained by VLS mechanism because the metal catalysts are not used in the synthesis.

Our results suggest the “self-catalytic VLS mechanism” as follows. The Zn film deposited by e-beam evaporation is composed of random grains with the diameter of 400 – 600 nm. When the Zn film is heated to 600 °C, the Zn film is melted and aggregated to form the Zn film since the melting point of Zn is 420 °C. At the same time, the ZnO (x < 1) is formed by the reaction of Zn and O2 in the air. As Zn becomes supersaturated, ZnO with small size is formed on the surface, which becomes the nuclei for the growth of nanowires [7, 11] and the long ZnO nanowires with high aspect ratio are formed via "self-catalyst". The growth model is schematically shown in Fig. 5.

![Image](image4.png)  

**Fig. 5** Growth model.

In summary, ZnO nanowires with wurtzite crystal structure were successfully synthesized by annealing the Zn films at 600 °C in the air prepared by e-beam evaporation. Nanowires of high aspect ratio with the diameter of 50 – 100 nm and the length of 5 – 10 μm were formed. This is a very simple method to synthesize ZnO nanowires without using any catalyst.

**References**

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![Fig. 4 TEM image (a) and selected area diffraction pattern (b) of ZnO nanowire synthesized by annealing Zn film at 600 °C in the air.](image)

4. SUMMARY

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![Fig. 5 Growth model.](image)

REFERENCES


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