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Formation and Size Control of ZnO Nanowires on Al-Zn-Si-Fe Alloy by Directed Melt Oxidation Process

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Abstract. Tetrapod like ZnO nanowires were formed by the directive melt oxidation of Al-Zn-Si-Fe alloy at the temperature over 1000°C in air. X-ray diffraction patterns revealed that the ZnO nanowires had wurtzite structure with the *c*-axis and *a*-axis lattice constants of 0.520 and 0.325 nm, respectively. The lattice constants are similar with those of ZnO single crystal. The size control of ZnO nanowires was achieved by varying the oxidation temperature and the amount of Zn in alloy. The lower the oxidation temperature was, the smaller was the diameter of the ZnO nanowires. And with decreasing the amount of Zn, it was diminished the diameter of the formed ZnO nanowires. The diameter was as small as 50 nm at the amount of Zn of 5 wt%.

Keywords: ZnO, nanowires, tetrapod shape, directive melt oxidation, size control

1. Introduction

Recently, nanoscale materials have attracted much attention due to their novel physical properties resulted from the restricted size. This gives rise to the potential application in electronic and optoelectronic nanodevices. The research on the nanoscale materials has been mainly carried out in the field of semiconductor including Si [1], Ge [2], GaN [3], GaAs [4], etc. Among them, the synthesis and characterization of ZnO nanowires have received much attention due to the potential application in nanoscale optoelectronic devices.

ZnO is one of the most attractive materials in optoelectronics due to its wide bandgap of 3.37 eV and large exciton binding energy of 60 meV. The wide bandgap of 3.37 eV is suitable for ultraviolet (UV) light emitting, which enables to use as UV light emitting devices. The large exciton binding energy of 60 meV, much greater than thermal energy at RT (24 meV), leads to an efficient excitonic emission of UV region even at room temperature (RT). At recent, the excitonic lasing action was reported in ZnO nanowires [5] as well as bulk ZnO materials, which has stimulated the studies on the synthesis and the application of ZnO nanowires.

Various methods, such as thermal evaporation [6], electrophoretic deposition [7], electrochemical etching [8], and electrochemical deposition [9], have been used to synthesize ZnO nanowires.

Here, we report a very simple method to produce large-scale ZnO nanowires by thermal oxidation of Al-Zn alloy at the temperature over 1000°C in air.

2. Experimental

ZnO nanowires were synthesized by thermal oxidation of Al alloy containing Zn, Si and Fe in air. The source material for the synthesis of ZnO nanowires was prepared by well mixing the Al alloy, the chemical compositions of which were Al base, 8 wt% Si, 0.25 wt% Zn, and 0.40 wt% Fe, and powder of pure Zn in an alumina crucible at 700°C. The four kinds of source alloys were prepared by varying the Zn content in the range of 3–10 wt%, respectively. Then the Al-Zn alloys were oxidized in a furnace in air. The oxidation

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was performed at the temperatures of 1050, 1100, and 1150°C in order to investigate the growth behavior of ZnO nanowires with oxidation temperature. The growth behavior of ZnO nanowires was examined at interval of 1 h during the oxidation at constant temperature. After cooling down to room temperature, white colored product was found on the surface of the oxidized Al-Zn alloy. The crystal structure of the product was analyzed using X-ray diffractometer with Cu K_α radiation. The surface morphology was observed using scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) spectroscope.

3. Results and Discussion

For the sample prepared by the oxidation of the source Al-Zn alloy containing the Zn content of 3 wt%, ZnO nanowires were not formed regardless of oxidation temperature and oxidation time. In case of the source Al-Zn alloys including the Zn amount above 5 wt%, ZnO nanowires started to produce during the oxidation at the temperature above 1000°C for 2 h in air.

X-ray diffraction (XRD) patterns were recorded to analyze the crystal structure of the ZnO nanowires. Figure 1 shows the XRD patterns of ZnO nanowires grown during the oxidation at 1150°C for 2 h using a source Al-Zn alloy to contain the Zn content of 5 wt%.

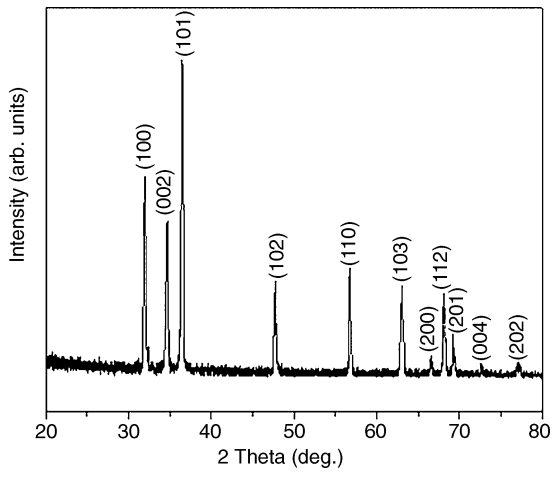

Fig. 1. XRD pattern of ZnO nanowires synthesized by directive melt oxidation of Al-5 wt% Zn alloy at 1150°C for 2 h.

The diffraction patterns can be well indexed to hexagonal structure of ZnO. The lattice constants of the ZnO nanowires are $a = 0.325$ nm, $c = 0.520$ nm, respectively, which is in well agreement with those of ZnO single crystal ($a = 0.324$ nm, $c = 0.519$ nm), indicating high crystallinity of the nanowires. In addition, no peaks from Zn and other impurities were detected in the pattern, which is also indicative of high quality ZnO. Similar XRD patterns were also taken for all other samples prepared at different oxidation temperatures. EDX spectra indicated that the nanowires were composed of only Zn and oxygen.

The morphology of the samples was observed by scanning electron microscope (SEM). Typical SEM image on the sample prepared at 1150°C for 2 h with a source Al-Zn alloy, in which the chemical composition of Zn is 5 wt%, is shown in Fig. 2. Tetrapod-shaped ZnO nanowires with four legs, extended from the center, are found in high yield and uniformly distributed on the whole surface. No other shaped crystals and powders are found. The high-resolution image (Fig. 2(b)) shows that the diameter and the length of the ZnO nanowires are about 50 nm and several tens of micrometers, respectively.

The influence of oxidation temperature and Zn content in source Al-Zn alloy on the size of nanowires was investigated using the source Al-Zn alloys to contain 5, 7, 10 wt% Zn, respectively. Figure 3 exhibits the SEM images of ZnO nanowires obtained during the oxidation of source Al-Zn alloys to contain (a) 5, (b) 7, (c) 10 wt% Zn, respectively. The oxidation was conducted in a furnace at 1150°C for 2 h in an air atmosphere. As the Zn content increases, the tetrapod shape of the nanowires is not changed and the size of the nanowires increases from the diameter of ~50 nm and the length of ~20 micometers, to the diameter of ~600 nm and the length of ~50 micometers.

The effect of oxidation temperature on the size of nanowires was also examined. Figure 4 shows the SEM images of the ZnO nanowires formed during the oxidation of source Al-10 wt% Zn alloys at (a)1050, (b)1100, and (c)1150°C for 2 h, respectively. The size of the ZnO nanowires increases from ~100 nm × ~15 micrometers to ~600 nm × ~50 micrometers. Higher temperature produces nanowires with larger diameter and longer length.

Figure 5 represents the variation of ZnO nanowire's size with oxidation temperature and Zn content. The

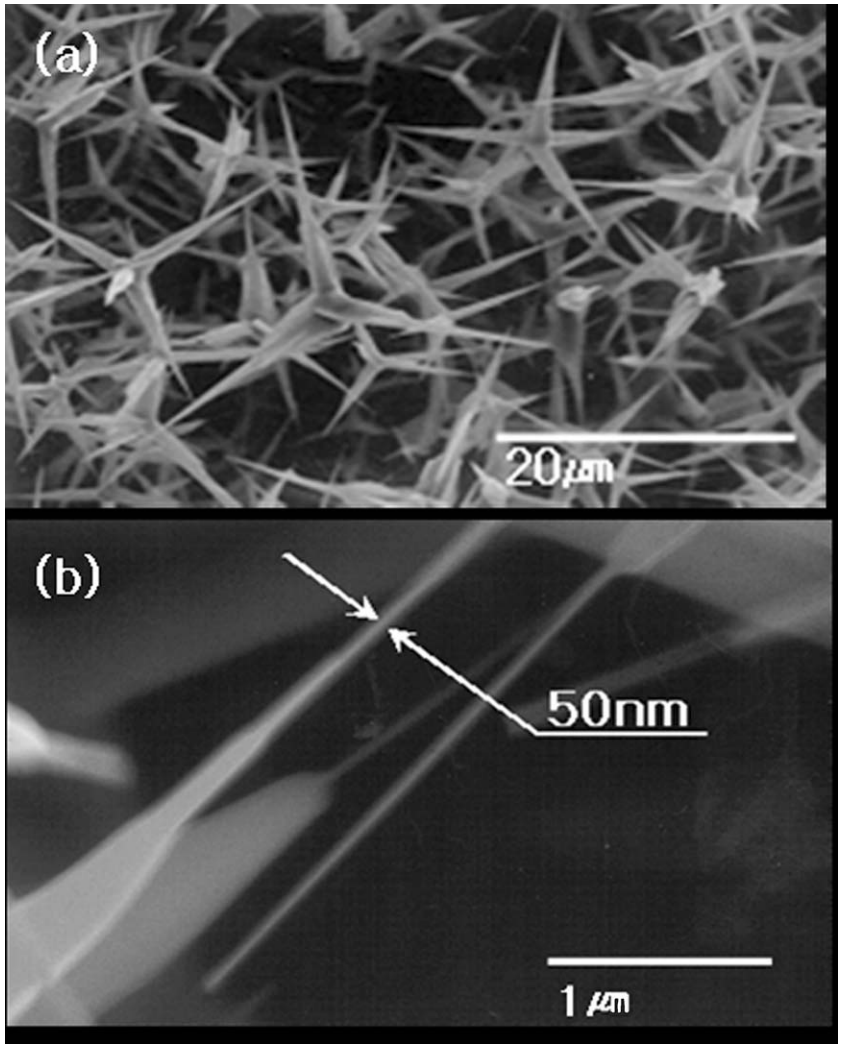

Fig. 2. SEM image of ZnO nanowires prepared by directive melt oxidation of Al-5 wt% Zn alloy at 1150°C for 2 h.

diameter increases when the oxidation temperature is changed from 1050 to 1100°C, while the diameter is maintained constantly over 1100°C. In case of the sample containing 5 wt% Zn, the diameter is not changed without regard to oxidation temperature.

From the fact that the tip of the nanowires is conical shape as shown in Fig. 2(b) and no aggregate is detected at the end of the nanowires, it is supposed that the growth of the nanowires proceeds in a vapor-solid (VS) mechanism. The growth model of conventional nanowires has been explained by vapor-liquid-solid (VLS) mechanism. The VLS growth process is connected with liquid-forming droplets. The nanowires grow through the liquid droplets due to supersaturation. Accordingly, the characteristic of the VLS growth mechanism is the existence of nanodroplets capped at the end of the nanowires [10]. However, in our case, any nanoparticles is not found at the tip of the nanowires, conforming that the nanowires grow via VS mechanism. Zn in source Al-Zn alloy is evaporated at our processing temperature over 1000°C because its boiling temperature is 911°C. Zn in vapor state reacts with oxygen atoms in air to yield ZnO molecules, which form the ZnO nuclei and grow to the ZnO nanowirs.

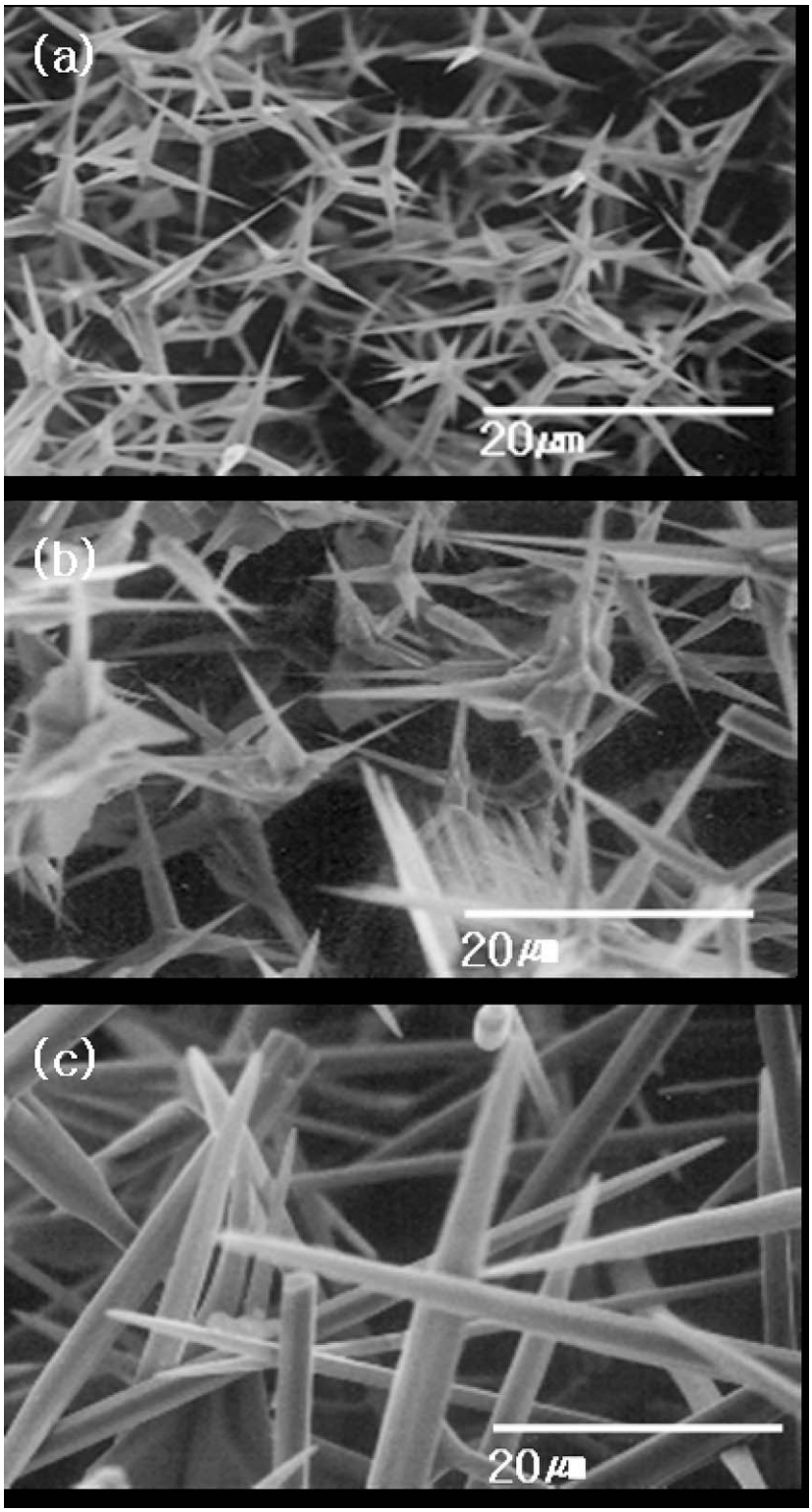

Fig. 3. SEM images of ZnO nanowires obtained during the oxidation of source Al-Zn alloys to contain (a) 5, (b) 7, (c) 10 wt% Zn.

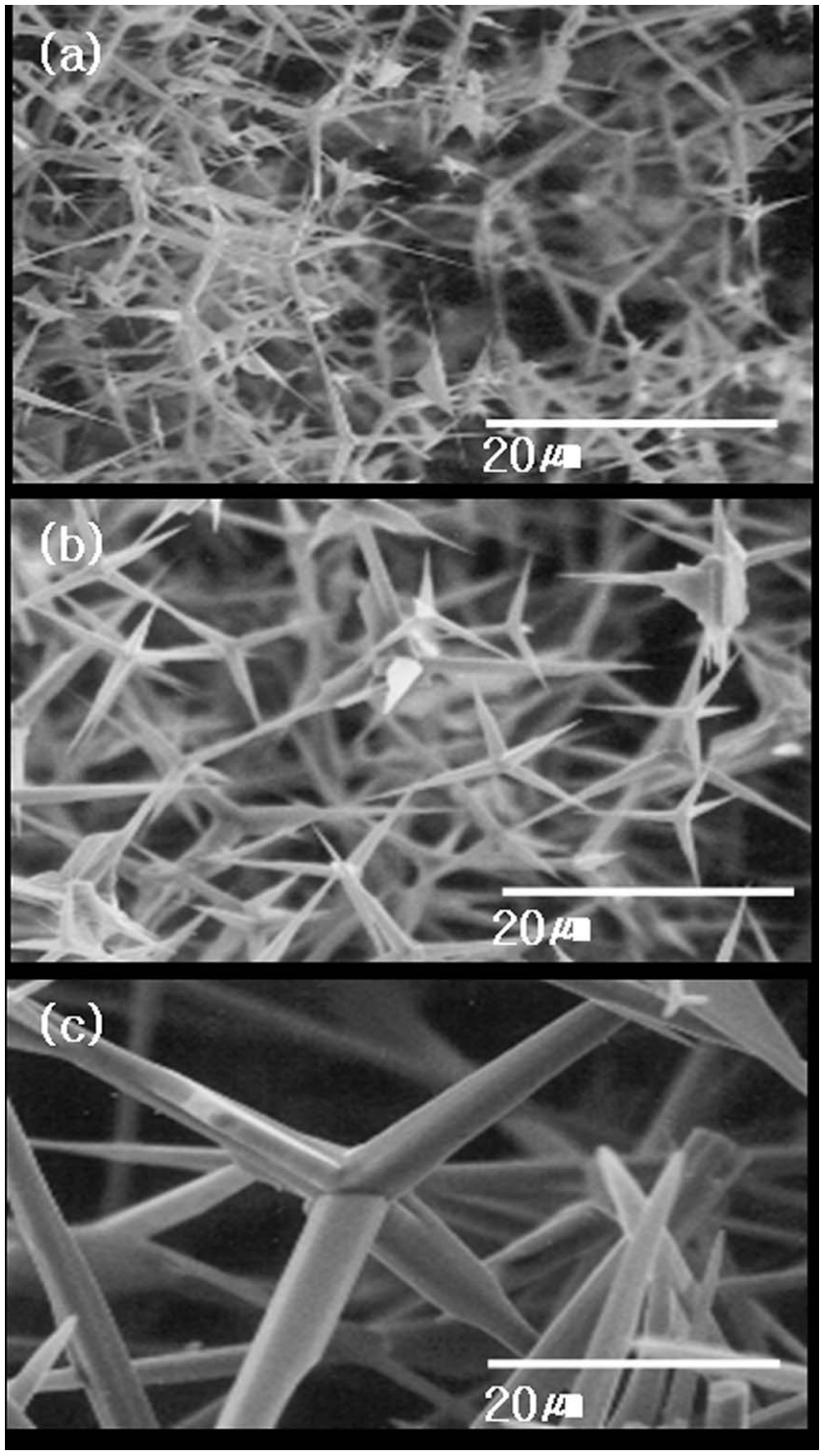

Fig. 4. SEM images of the ZnO nanowires formed during the oxidation of source Al-10 wt% Zn alloys at (a) 1050, (b) 1100, and (c) 1150°C for 2 h.

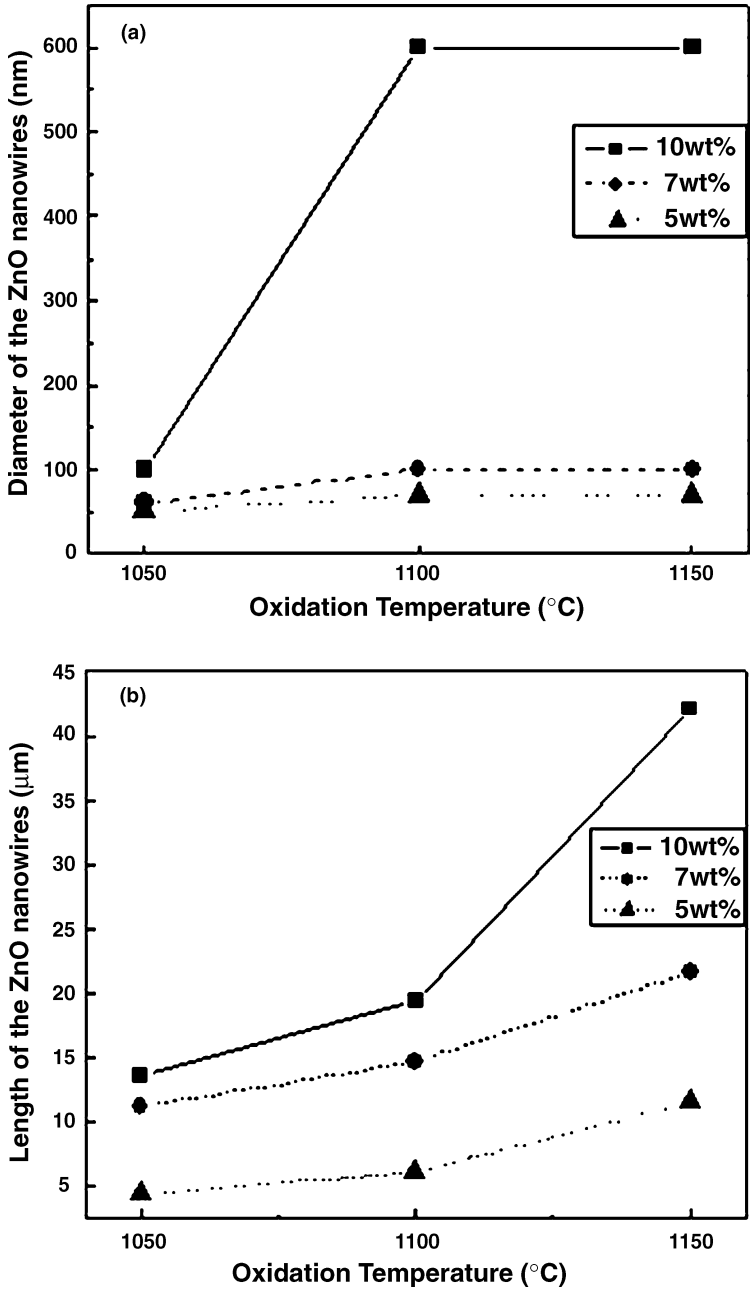

Fig. 5. Variation of ZnO nanowire's size with oxidation temperature and Zn content.

4. Conclusions

Highly crystalline ZnO nanowires have been successfully produced using the simple thermal oxidation of Al-Zn alloy above 1000°C in air. This is a practical and economical method to synthesize ZnO nanowires in high yield. The nanowires were single crystallines with hexagonal structure. The shape of the nanowires was tetrapod type. The growth proceeded via VS process. The diameter and the length control of the nanowires

were achieved by varying the oxidation conditions. With lowering the oxidation temperature and Zn content in source Al-Zn alloy, the longer oxidation time was necessary to produce the ZnO nanowires, whereas a further decrease in the diameter of the nanowires was achieved. The diameter was controlled to 50 nm and the length to 50 micrometers. Recently, it is well known that ZnO nanowires with tetrapod shape have very useful properties such as semiconductivity, wear resistance, vibration insulation, and microwave absorption. Thus it is expected the wide application of tetrapod ZnO nanowires as functional and structural materials in various fields including optoelectronics.

Acknowledgments

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