Large Area Synthesis of 1-D ZnO Nanostructure Arrays on Zn Substrate via Solvothermal Process

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Abstract. Large areas of one-dimensional ZnO nanostructures (nanorods and nanowires) were prepared by simple solvothermal method. The synthesis involves a template-less and surfactant free aqueous methods. In this study, Zn metal sheet was used as both Zn^{2+} ion source for the growth of ZnO nano-structures and substrate for oxide film. The mixed solvent of 1-propanol with water was used as solvents for nanorods and ethylene glycol with water was for nanowires. The solvothermal treatment of a zinc metal plate with the solvents at the temperature of 125 °C for 10 hours resulted in the 1-D ZnO nanostructures, which were grown on the Zn metal sheet. The synthesized ZnO was well aligned on whole area of substrate and the nanorods were 150 nm in diameter and 3 μm in lengths, respectively.

Introduction

Zinc oxide (ZnO) has been used in various technologies as varistor, acoustic wave filters gas sensor, catalyst, pigment, etc [1-3]. These various applications of ZnO are due to the specific chemical, surface and micro-structural properties of ZnO can be modified by introducing changes into the procedure of its chemical synthesis. Nowadays, growing interest in one-dimensional oxide nanomaterials, especially ZnO nanowires, is being displayed. ZnO, as a wide bandgap (3.37 eV) semiconductor with a large exciton binding energy (60 meV), has been extensively investigated, due to its promising applications in short wavelength light emitting, transparent conductor, piezoelectric materials and room temperature ultraviolet (UV) lasing. Recently, numerous studies on ZnO nanowires prepared by thermal evaporation [4-6], anodic alumina membrane templates, physical vapor deposition approaches [7] and wet chemical processes [1,8-10]. Especially, thermal evaporation method made a well aligned ZnO nanowire on sapphire substrate. However, the preparation methods mentioned above involve complex procedures, sophisticated equipment and rigorous experimental conditions. Therefore, it is necessary to develop a simple synthetic method to prepare well aligned ZnO nanorods for promising wide range applications.

In this study, we report the simple synthesis method for the aligned ZnO nanorods and nanowires on a large area of substrate using the solvothermal process. The solvothermal process was conducted with zinc metal plate and the mixed solvents at relatively low temperature of 125 °C.

Experimental Procedure

A polished Zn metal plate (10 mm x 10 mm x 1mm) was placed on teflon liner for hydrothermal vessel. Then the liner was filled with 60 ml of the mixed solvent, i.e., water with an alcohol. Several kinds of alcohols and polyols were examined to use for the synthesis of 1-D zinc oxide nano structures. In various experiment conditions, aligned 1-D zinc oxide nanorods were synthesized in

1-propanol (99.5%, Junsei Chemical, Japan) with water and the nanowires were synthesized in ethylene glycol (98%, Aldrich) with water. In each case, the ammonia solution (28 wt%, Junsei Chemical, Japan) was added into the container to adjust pH and to control the reaction rate. The solvothermal synthesis was conducted at 125 ^{o}C for 10 hours. After the reaction the synthesized ZnO on Zn substrate was dried in a convection oven (60 ^{o}C) for 6 hrs. The phase of synthesized nanostructures was confirmed with X-ray diffractometer (XRD, D/MAX-IIIC, Rigaku, Japan) and the morphologies were examined with scanning electron microscopy (SEM, XL30, FEG, Philips, Netherlands) and transmission electron microscopy (TEM, JEM 3010, JEOL, Japan).

Results and Discussion

Reaction Mechanism. In general, zinc metal dissolves in base solution as ion and forms $Zn(OH)_4^{2-}$ complexes. These complexes grow to the nuclei of appropriate size to dehydrate. Under solvothermal condition, the $Zn(OH)_4^{2-}$ complexes dehydrate to produce ZnO [11]. This procedure can be written as follows:

$$Zn \rightarrow Zn^{2+} + 2e^{-} \text{ (dissolution)} \tag{1}$$
$$Zn^{2+} + 4(OH)^{-} \rightarrow Zn(OH)^{4-} \text{ (complex)} \tag{2}$$
$$Zn(OH)_4^{2-} + Zn \rightarrow 2ZnO + 2H_2O + 2e^{-} \text{ (nucleation and growth)} \tag{3}$$

At the stage of zinc dissolution, the solubility of zinc to solvent varies as the solvent change. As the difference of dissolved zinc ions cause the difference of the zinc oxide product. And the chain of alcohol and the viscosity of solvents can affect the morphology and size of the synthesized nanostructures [12-15]. But the detailed role of solvents is not yet fully understood in this study.

Nanostructures of 1-D zinc oxide. The zinc oxide nano-rods and wires were prepared by simple solvothermal process. Figure 1 shows the low magnification SEM image of the synthesized zinc oxide nano-structures on large area of zinc substrate: (a) nanorods, (b) nanowires. The zinc oxide nanorods were synthesized with the mixed solvent of 1-propanol (40 ml), water (20 ml), ammonia (10 ml). The nanowires were synthesized with the mixed solvents of ethylene glycol (5 ml), water (60 ml), ammonia (5ml). Both of the samples are covered with the zinc oxide nanostructures on whole area of zinc substrate uniformly.

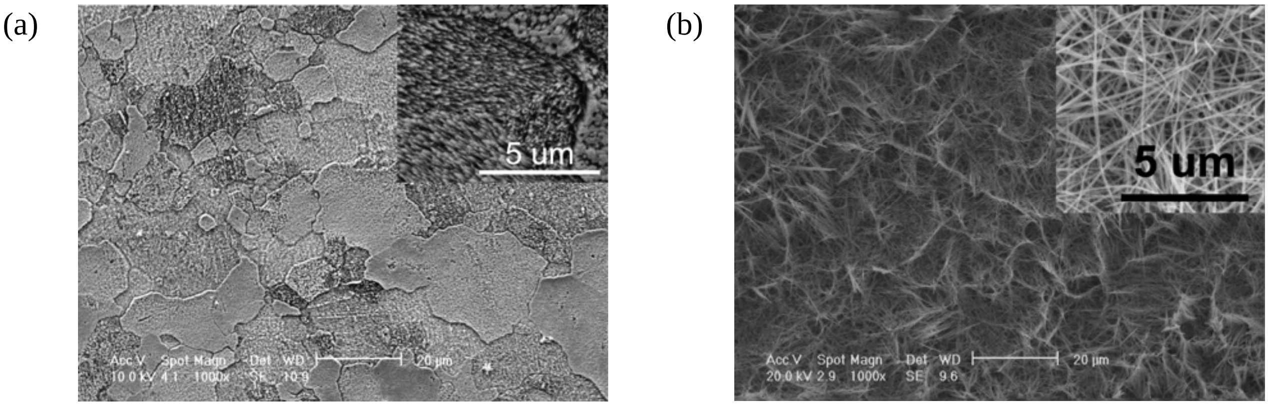

Fig.1. Low magnification SEM images of synthesized zinc oxide under solvothermal conditions at 125 ^{o}C: (a) nanorods (1-propanol/water solvent) and (b) nanowires (Ethylene glycol/water solvent).

Figure 2 shows the high magnification of the synthesized zinc oxide nanostructures with SEM image and TEM micrograph inset. The synthesized nano-rods were well-aligned on zinc substrate and the diameter of the rods about 150~200 nm and the length was about 2~3 μm. The end-tip shape of rods were almost flat and some prismatic. The synthesized nano-rods were well-aligned on zinc substrate and the diameter of wires about 120 nm and the length was about above 10 μm. And the wires had the sharp end-tip. The shape and the aspect ratio of the zinc oxide nano-structures were changed as the different solvent composition.

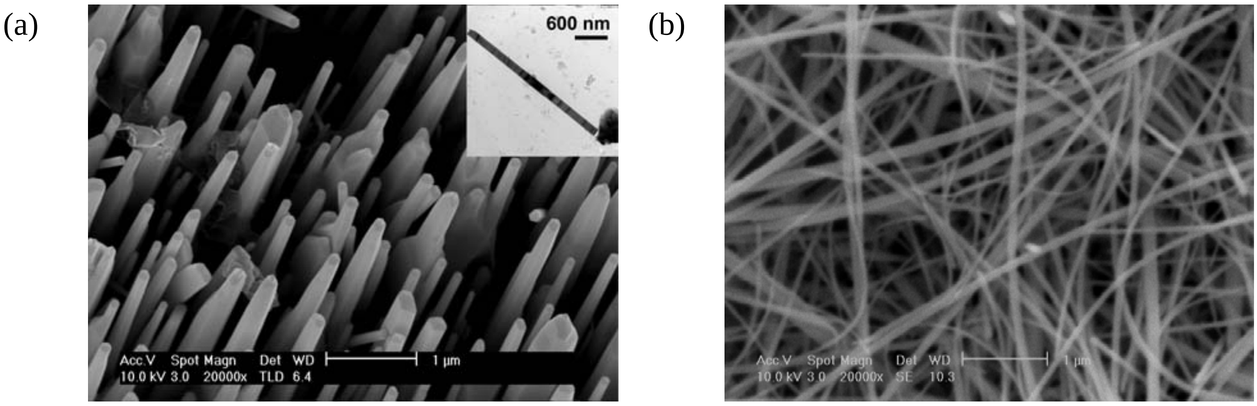

Fig.2. High magnification SEM images and TEM image (inset) of synthesized zinc oxide under solvothermal conditions at 125 °C: (a) zinc oxide nanorods (1-propanol/water solvent) and (b) zinc oxide nanowires (ethylene glycol/water solvent).

Characteristics of ZnO nanostructures. The phases of synthesized zinc oxide nanostructures were analyzed by X-ray diffraction analysis. Figure 3(a) shows the XRD pattern of initial zinc metal which acts as both Zn ion source and substrate and Figure 3(b) shows the XRD pattern of synthesized zinc oxide nano-rods while Figure 3(c) shows the patterns of zinc oxide nano-wires. All the obtained zinc oxide nanostructures are of wurtzite structure (hexagonal phase, space group P6m$_3$mc). And the patterns of synthesized ZnO nanostructures are in good agreement with the typical zincite patterns (JSPDS 36-1451, a=3.248 Å, c=5.206 Å) but there are still remain zinc substrate's peak. At the pattern of zinc oxide nano wires has higher relative intensity of the (002) peaks.

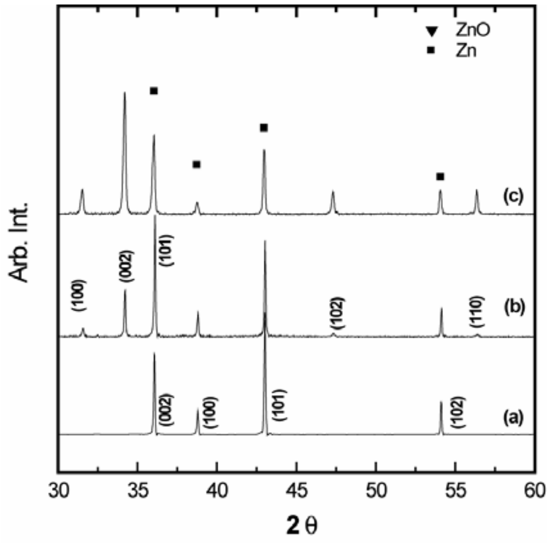

Fig.3. XRD patterns of (a) initial Zn substrate; (b) zinc oxide nanorods on zinc substrate; (c) zinc oxide nanowires on Zn substrate

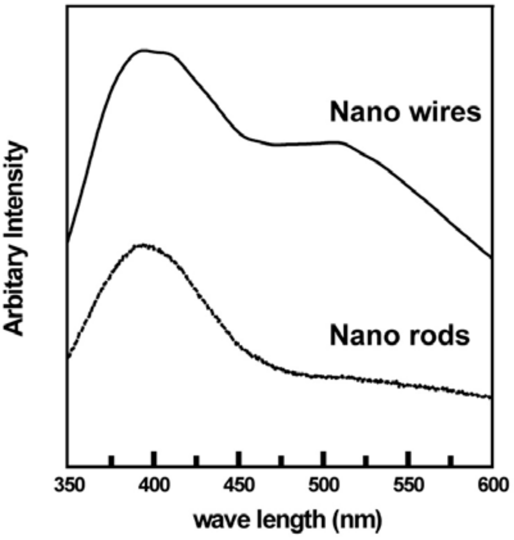

Fig.4. Room Temperature photoluminescence spectrum of synthesized nano-rods and nanowires

Figure 4 shows the room-temperature photoluminescence of the nanostructures was measured using a Xe lamp with the excited wavelength of 325 nm. The spectrum of zinc oxide nanowire consists of a strong UV emission and a weak green emission while the spectrum of nanorod shows only UV emission. The UV emission, located at 390 nm, is the exciton recombination related near-band edge emission (NBE) of ZnO and the green band with the center wavelength at about 510 nm is from the recombination of electrons at conduction band with holes trapped in oxygen-related defects[6].

Summary

Zinc oxide nanorods with diameters of 150 nm and length of 3 μm, wires with diameters of 120 nm and length of above 10 μm were synthesized on the large area of zinc substrates through a simple solvothermal method. The nanorod had a flat end and the nanowires had sharp tips. The well-aligned zinc oxide structures could be simply controlled with change of the solvent in solvothermal synthesis.

The growth direction of the zinc oxide nanostructures was [0001] direction. Dissolution-nucleation-growth mechanism was suggested for the formation of the zinc oxide nanostructures.

Acknowledgments

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References

[1] L. Vayssieres: Adv. Mater. Vol. 15 (2003), p. 464-466

[2] E. A. Meulenkamp: J. Phys. Chem. B Vol. 102 (1998), p. 5566-5572

[3] L. Dong, Z. Cui, and Z. Zhang: Nanostructured Materials Vol. 8 (1997), p. 815-823

[4] S. Li, C. Lee, and T. Tseng: J. Cryst. Growth Vol. 247 (2003), p. 357-362

[5] H. Yan, R. He, J. Pham, and P. Yang: Adv. Mater. Vol. 15 (2003), p. 402-405

[6] U. Manzoor and D. K. Kim: Scripta. Mater, Vol. 54 (2006), p. 807-811

[7] M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, and P. Yang: Adv. Mater. Vol. 13 (2001), p. 113

[8] L. Guo, J. Cheng, X. Li, Y. Yan, S. Yang, C. Yang, J. Wang, and W. Ge: Mat. Sci. Eng. C-Bio. S Vol. 16 (2001), p. 123-127

[9] D. Boyle, K. Govender, and P. O'Brien: Chem. Comm. (2002), p. 80-81

[10] B. Liu and H. Zeng: J. Am. Chem. Soc. Vol. 125 (2003), p. 4430-4431

[11] W. J. Li, E. W. Shi, W. Z. Zhong, and Z. W. Yin: J. Cryst. Growth. Vol. 203 (1999), p. 186-196

[12] H. G. Choi, Y. H. Jung, and D. K. Kim: J. Am. Ceram. Soc. Vol. 88 (2005), p. 1684-86

[13] B. Cheng and E. T. Samulski: Chem. Comm. (2004), p. 986-987

[14] A. L. Pan, R. B. Liu, S. Q. Wang, Z. Y. Wu, L. Cao, S. S. Xie, and B. S. Zou: Journal of Crystal Growth Vol. 282 (2005), p. 125-130

[15] E. M. Wong, J. E. Bonevich, and P. C. Searson: J. Phys. Chem. B Vol. 102 (1998), p. 7770-7775