Hydrothermal Growth of ZnO Nanostructures Using Zinc Thin Films as Seed Layer

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ABSTRACT

Zinc oxide nanostructure is selectively synthesized by a simple reaction of zinc acetate dehydrate. With hexamethyltetramine (HMT) under mild hydrothermal conditions, we use zinc thin films as seed layer. Scanning electron microscopy (SEM) result shows that zinc thin films were oxidized to hexagonal ZnO seeds in the absence of zinc salt and base under hydrothermal conditions. The effect of a mixed water/ethanol solvent with various ethanol contents on the morphology, nanostructure, and compositional properties of the synthesized zinc oxide is examined. SEM studies show that the ZnO pillar and wire structures could be obtained at low ethanol contents, while high ethanol contents are favorable for the formations of ZnO thin film structures through coalescence of adjacent rods. X-ray diffraction (XRD) studies show that the phenomenon of crystal tilt appeared as the ethanol content increases. Results indicate that the ethanol could acts as a shape inducing molecule. Mechanism of the growth of different ZnO nanostructures using zinc thin films as seed layer and various ethanol contents in a mixed water/ethanol solvent are also discussed.

Keywords: Hydrothermal, Zinc oxide, Seed, Mixed solvent, Nanostructures

1 INTRODUCTION

Zinc oxide is an excellent compound semiconductor for electronic and photonic applications due to its wide direct band-gap (3.37 eV). ZnO have been widely applied in high technology fields such as photodetectors [1], surface acoustic wave devices [2], photonic crystals [3], light-emitting diodes [4], photoelectrodes [5], gas sensors [6] and transparent conductive coating [7].

ZnO nanostructures can be grown via solution [8] or from gaseous route [9]. The routes mentioned above for the synthesis of ZnO nanostructures, the hydrothermal synthesis [10] is one of the most promising routes due to its low-cost and adjustable growth conditions. In recent years, Several ZnO nanostructures such as nanowires, rods, nanotubes, nanobelts, and nanoflowers have been synthesized via hydrothermal solution processes [11-17]. Seeds are needed to facilitate ZnO nanostructures growth on a substrate. Generally, ZnO seeds are prepared either by thermal decomposition of zinc salts or pre-synthesized ZnO seeds deposited on the substrate. However, uniformity of the ZnO seeds on the substrate is poor via the methods mentioned above. In the paper, ZnO nanostructures were prepared from the mixed water/ethanol solution of zinc acetate dihydrate and hexamethyltetramine (HMT) under hydrothermal conditions using pre-deposited zinc as seeds for ZnO growth. The morphology, crystal, structure, and mechanism of the ZnO nanostructures were investigated.

2 EXPERIMENTAL

Hydrothermal synthesis of ZnO nanowire arrays was carried out by suspending a Zn-deposited (100 nm) wafer upside-down in a PTFE bottle filled with 50 mL mixed water/ethanol solvent with various ethanol contents containing zinc acetate dihydrate (25 mM) and hexamethyltetramine (25 mM). The PTFE bottle was put in a pre-heated oven at 90°C for 5 h. The wafer was then removed from solution, rinsed with deionized water, and dried with an air stream.

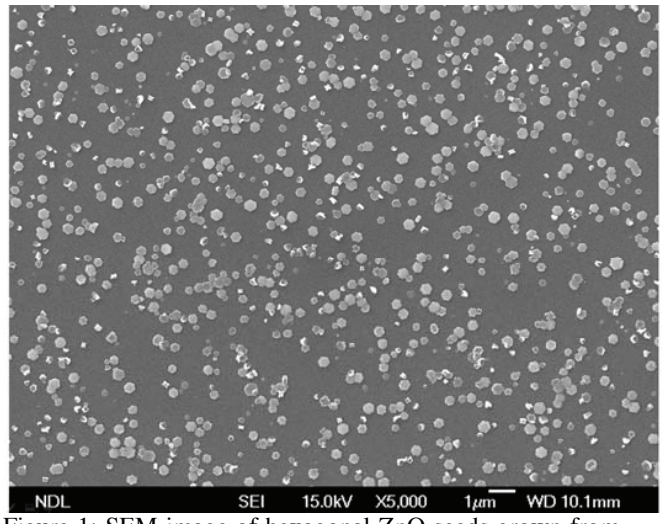
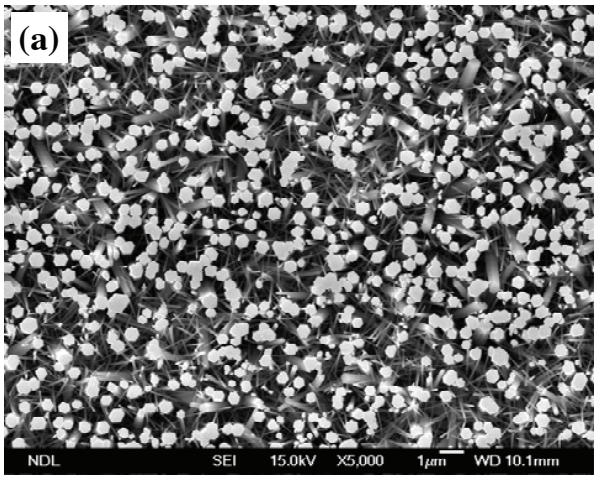


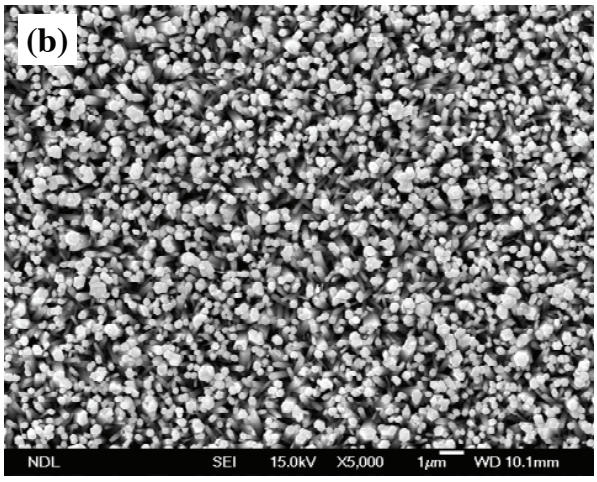
Figure 1: SEM image of hexagonal ZnO seeds grown from zinc thin films by hydrothermal route.

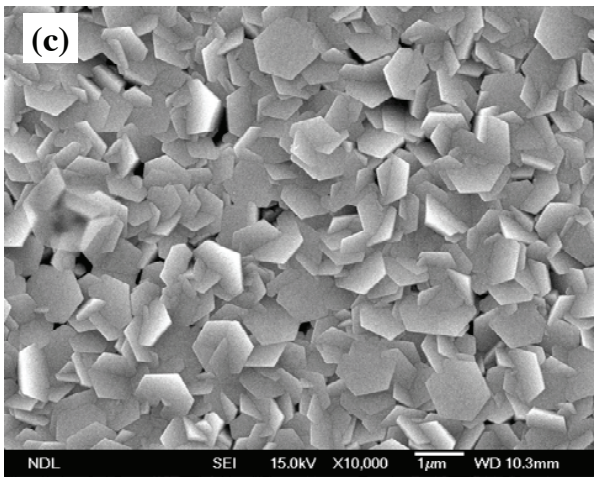
3 RESULTS AND DISCUSSION

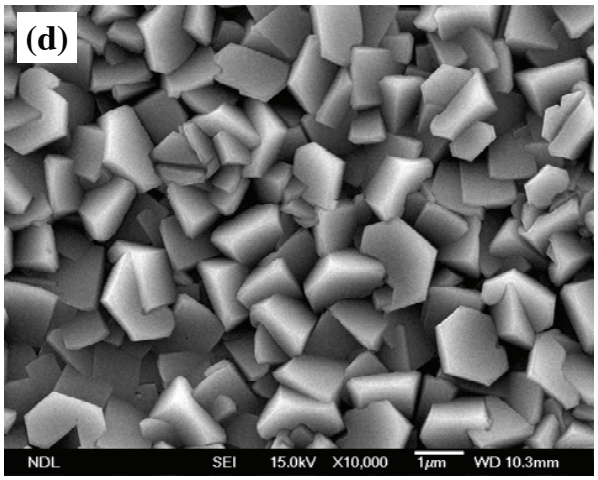
To prepare the ZnO seeds for the hydrothermal growth of ZnO nanostructures, Zn-deposited wafer was immersed in water at 90°C for 1 h in the absence of precursors. Figure 1 shows the surface morphology of the treated wafer. Hexagonal particles appear on the substrate, indicating the zinc was oxidized to zinc oxide upon hydrothermal treatment. The ZnO particles were used as seeds for subsequent growth of ZnO nanostructures.

Figure 1 shows the surface morphology of ZnO nanostructures grown at various ethanol contents. ZnO nanowires were grown on the substrate, as shown in Fig. 2(a), which consist of both thick and thin nanowires. With the addition of ethanol, thin nanowires disappear and dense nanowires array is formed, as shown in Fig. 2(b). With further addition of ethanol content, no wires but hexagonal plates morphology with different thickness were found (Fig.









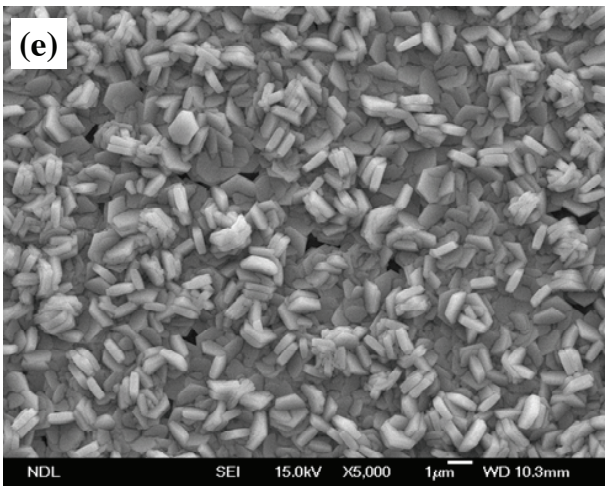


Figure 2: SEM images of ZnO thin films deposited at various water/ethanol ratios (V/V, mL): (a) 50/0, (b) 40/10, (c) 30/20, (d) 20/20, and (e) 10/40.

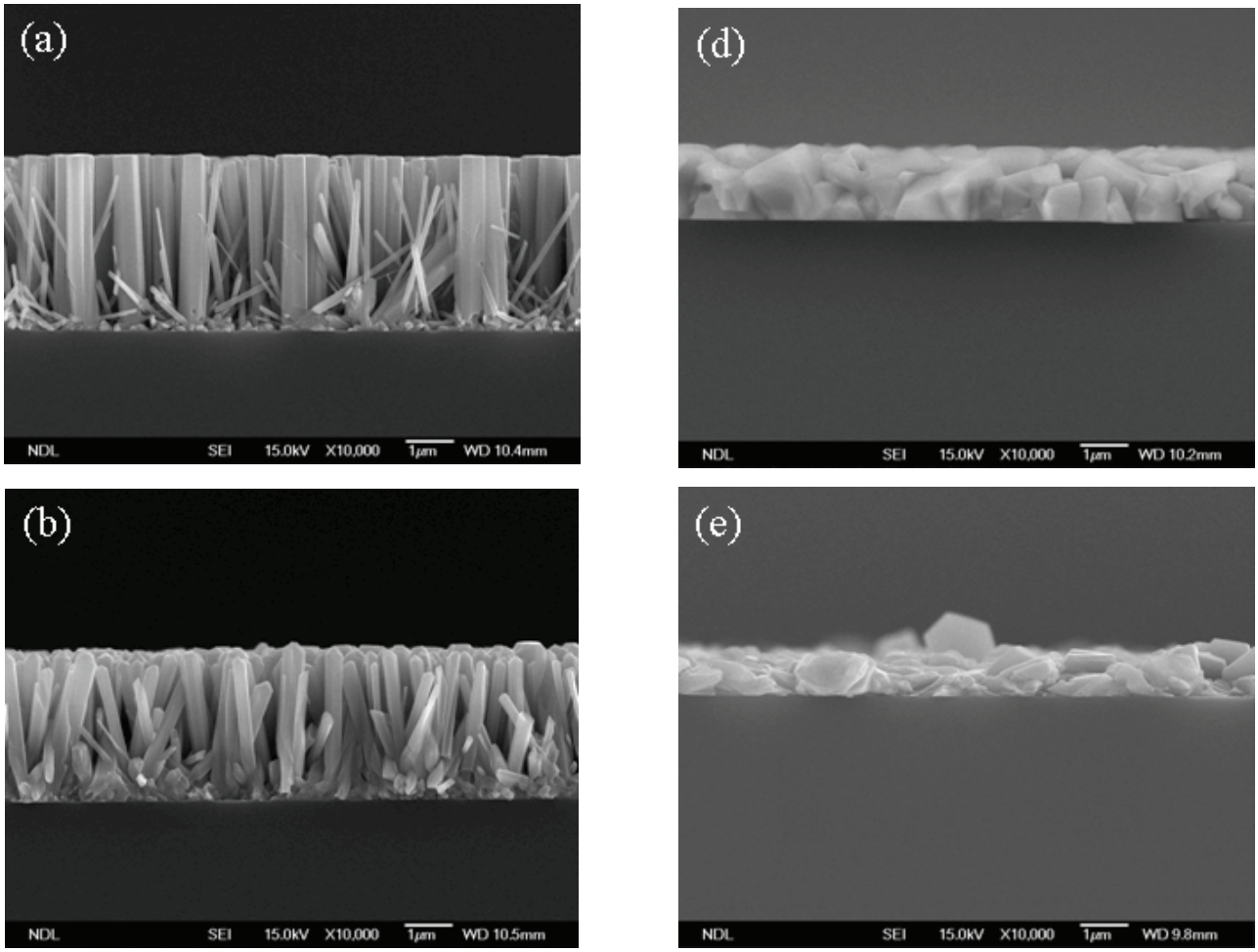


Figure 3: Cross-sectional SEM images of ZnO thin films deposited at various water/ethanol ratios (V/V, mL): (a) 50/0, (b) 40/10, (c) 30/20, (d) 20/20, and (e) 10/40.

2(c)-(e)). Figure 3 shows the cross-sectional SEM images of ZnO nanostructures grown at various ethanol contents. Both thin and thick nanowires were found, and the top of the nanowires is smooth (Fig. 3(a)). After addition of ethanol, the top of the nanowires exhibits pyramid-like

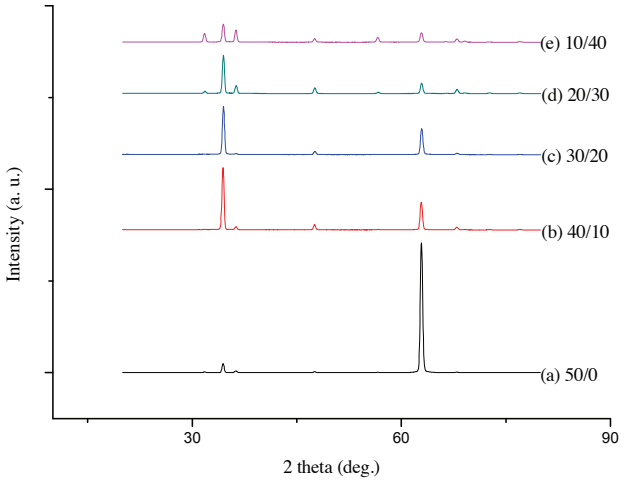


Figure 4: XRD patterns of ZnO thin films deposited at various water/ethanol ratios (V/V, mL): (a) 50/0, (b) 40/10, (c) 30/20, (d) 20/20, and (e) 10/40.

morphology (Fig. 3(b)). With further addition of ethanol content, isolated nanowires coalesce to form thin films with different densities, as shown in Fig. 3(c)-(e). The growth and decline of the measured XRD peaks also reveal that the crystal tilting occurs as addition of ethanol. The XRD θ-2θ scan spectra shown in Figure 4, the strongest diffraction peak is switched from (103) to (002) with increasing ethanol content. Based on the observation of ZnO crystal growth and morphology evolution, a rational mechanism for the ZnO morphology evolution is proposed. When the Zn-coated wafer was put into the growth solution, the metal surface is oxidized to $Zn(OH)_2$, and the $Zn(OH)_2$ is subsequent dehydrated upon heating to form ZnO. The chemical reactions to form ZnO nanorods are formulated as follows:

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2 \quad (1)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (2)$$

Oxidation of zinc leads to the formation ZnO seeds in the initial stage. The ZnO seeds facilitate the formation of loose ZnO nanowires array. The thin nanowires dissolve to form tiny nuclei during crystal growth process, and the nuclei recrystallize to form thick nanowires. The dissolution-recrystallization process thus results in the formation of thick ZnO nanowires. The ethanol content in the mixed solvent also plays an important role on the morphology evolution of the ZnO nanostructures. Wang et al. indicate that the increasing ethanol contents can accelerate crystal tilting [18]. Therefore, the increasing ethanol contents lead to crystal coalescence and thicknesses reduction of the ZnO thin films.

4 CONCLUSIONS

The hydrothermal growth of ZnO nanostructures using zinc thin film as seed layer has been investigated. ZnO seeds could be in situ formed on the substrate. The effect using mixed solvent for the hydrothermal growth of ZnO nanostructures thin film was also investigated. The ZnO wire structures could be obtained at low ethanol contents, while high ethanol contents were favorable for the formations of ZnO thin film structures through coalescence of adjacent wires. The oxidation-dissolution-recrystallization mechanism has been proposed to illustrate the morphology evolution of ZnO nanostructures.

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REFERENCES

[1] S. Liang, H. Sheng, Y. Liu, Z. Huo, Y. Lu and H. Chen, "ZnO Schottky ultraviolet photodetectors", J. Cryst. Growth, 225**,** 110, 2001.

[2] W. C. Shih and, M. S. Wu, "Growth of ZnO films on GaAs substrates with a SiO_2 buffer layer by RF planar magnetron sputtering for surface acoustic wave applications", J. Cryst. Growth, 137, 319, 1994.

[3] Y. F. Chen, D. Bagnall and T. F. Yao, "ZnO as a novel photonic material for the UV region", Mater. Sci. Eng. B 75**,** 190, 2000.

[4] N. Saito, H. Haneda, T. Sekiguchi, N. Ohashi, Sakaguchi, I. and K. Koumoto, "Low-Temperature Fabrication of Light-Emitting Zinc Oxide Micropatterns Using Self-Assembled Monolayers", Adv. Mater., 14, 418, 2002.

[5] J. Y. Lee, Y. S. Choi, J. H. Kim, M. O. Park and S. Im, Thin Solid Films, "Optimizing n-ZnO/p-Si heterojunctions for photodiode applications", 403**,** 553, 2002.

[6] A. Mitra, A. P. Chatterjee and H. S. Maiti, Mater. Lett. "ZnO thin film sensor", 35, 33, 1998.

[7] Gordon, R. G. MRS Bull., "Criteria for choosing transparent conductors", 25, 52. 2000.

[8] M. Izaki and T. Omi, "Transparent zinc oxide films prepared by electrochemical reaction", Appl. Phys. Lett., 68, 2439, 1996.

[9] S. Fay, L. Feitknecht, R. Schluchter, U. Kroll, E. Vallat-Sauvain and A. Shah, "Rough ZnO layers by LP-CVD process and their effect in improving performances of amorphous and microcrystalline silicon solar cells", Sol. Energy Mater. Sol. Cells, 90, 2960, 2006.

[10] C. S. Cundy and P. A. Cox, "The hydrothermal synthesis of zeolites: History and development from the earliest days to the present time", Chem. Rev., 103, 663, 2003.

[11] Z. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie and M. J. Mcdermott, "Biommetic arrays of oriented helical ZnO nanorods and columns", J. Am. Chem. Soc., 124, 12954, 2002.

[12] Z. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie, M. J. Mcdermott, M. A. Rodriguez, H. Konishi and H. F. Xu, "Complex and oriented ZnO nanostructures", Nature Mater., 2, 821, 2003.

[13] L. Vayssieres, K. Keis, S. E. Lindquist and A. Hagfeldt, "Purpose-built anisotropic metal oxide material: 3D highly oriented microrod array of ZnO", J. Phys. Chem. B, 105, 3350, 2001.

[14] L. Vayssieres, K. Keis, A. Hagfeldt and S. E. Lindquist, "Three-dimensional array of highly oriented crystalline ZnO microtubes", Chem. Mater., 13, 4395, 2001.

[15] L. Vayssieres, "Growth of arrayed nanorods and nanowires of ZnO from aqueous solutions", Adv. Mater., 15, 464, 2003.

[16] L. E. Greene, M. Law, J. Goldberger, F. Kim, J. C. Johnson, Y. F. Zhang, R. J. Saykally and P. D. Yang, "Low-Temperature Wafer-Scale Production of ZnO Nanowire Arrays", Angew. Chem., Int. Ed., 42, 3031, 2003.

[17] J. Zhang, L. D. Sun, C. S. Liao and C. H. Yan, "A simple route towards tubular ZnO", Chem. Commun., 3, 262, 2002.

[18] M. S. Wang, E. J. Kim, E. W. Shin, J. S. Chung, S. H. Hahn and C. H. Park, J. Phys. Chem. C, "Low-temperature solution growth of high-quality ZnO thin films and solvent-dependent film texture", 112, 1920, 2008.