# The Morphology and Evolution of Zinc Oxide Flowers Like By Direct Synthesis and Sequential Nucleation Growth

N. Elizondo<sup>\*, \*\*</sup>, R. Obregón<sup>\*\*</sup>, E. Pérez<sup>\*\*</sup>

\*Department of Materials Science & Engineering, University of North Texas at Denton, TX 76203, USA, 940.369.7591 Fax:

940.565.4824 Tel: nelizond@yahoo.com

\*\*Department of Physics, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, N. L., CP 66451, México

# ABSTRACT

The morphology evolution characteristics of ZnO nanostructures were systematically studied from dense rods to ZnO flowers like. The ZnO flowers like were prepared by direct decomposition of a Zn(OH)<sub>4</sub><sup>2-</sup> precursor and by the sequential nucleation growth method consisted of a multistep synthesis of complex nanostructured films. Systematical condition-dependent experiments were compared to reveal the formation and detailed growth process of ZnO nanosized crystallites and aggregates. The experimental results studied by Xray diffraction, transmission electron microscopy, and scanning electron microscopy indicated that the precursor, solution basicity, reaction temperature and pressure as well as time were responsible for the variations of the morphologies. ZnO flowers like and large nanorods of exceptional uniformity, orientational alignment, and optical properties have been produced in this work.

*Keywords*: zinc oxide flowers like, synthesis, morphology, evolution, characterization

# INTRODUCTION

One-dimensional nanometer-sized semiconductor materials, i.e., nanowires and nanorods, have attracted considerable attention due to their great potential for fundamental studies of the roles of dimensionality and size in their physical properties as well as for their application in optoelectronic nanodevices [1]. Zinc oxide (ZnO), a semiconductor with a direct wide band gap (3.37 eV at room temperature) and large exciton binding energy (60 meV), is one of the most promising materials for the fabrication of optoelectronic devices operating in the blue and ultraviolet (UV) region and for sensing applications [2]. The synthesis, gas characterization and application of various 1D ZnO nanostructures including the rods/wires [3], belts/ribbons [4], rings [5], tetrapods [6], combs [7], sheets [8] and complex structures [9] are presently the subject of intense research.

During the past decades, reports on the synthesis of various structures of ZnO have increased rapidly, including rods [10], wires [11], tubes [12], tower- [13], star- [14], dendrite- [15], and flower-like [16] and [17]. These structures are expected to have more potential applications in building functional electronics devices with special architectures and distinctive optoelectronic properties. Therefore, it is desired to synthesize ZnO nano- or microstructures in a controllable shape and size by simple approach to answer the demand for exploring the potentials of ZnO. Unfortunately, up to now, it is still challenging task for material scientists to directly fabricate large-scale ZnO crystals with controlled morphology. The ability to control and manipulate the physical and chemical properties of materials has been one of the challenging issues for chemistry and materials researchers. These properties are strongly related to two crucial geometrical parameters: size and shape. Now, chemists are exploring many ways to obtain such control at the nanometer scale. Various shapes of materials have been synthesized, such as nanotube, nanorod, nanobelt, nanoplate, and nanoparticles, flower-like Recently, three-dimensional pattern, etc. (3D) superstructures composed of 1D and 2D nanoscale building blocks have been the subject of increasing interest in material synthesis and device fabrication because of their unique collective properties and practice applications [18-20]. Self-assembly process is probably the simplest synthetic route to 3D superstructure [21]. The hydrothermal technique is a useful method in preparing nanomaterials and it has been applied to the synthesis of various ZnO nanostructures. The conditions for synthesizing ZnOnanorod arrays from aqueous solutions were recently reviewed by Govender et al.,[22] and similar aqueous chemical routes have been developed to grow oriented arrays of nanorods and nanotubes of other metal chalcogenides and hydroxides.[23-27] Electrochemical deposition in aqueous solutions has also been applied to directly deposit oriented films of ZnO nanorods, [28-33] cuprous oxide nanocubes, nanopyramids,[34] and several other crystal habits.[35] To date, most of these solutionphase synthesis methods have produced either continuous film structures or arrays of nanorods or nanotubes. Although a few studies have recently reported tower-, tube-, and flower-like morphologies resulting from the addition of organic growth modifiers,[36-38] fabrication of more complex nanostructures, such as those observed in natural materials or biominerals,[39] remains a significant challenge.

### **EXPERIMENTAL SECTION**

The ZnO flowers like were synthesized mainly by modification of two methods: the first method is the Direct Method (DM) and the second is the Sequential Nucleation and Growth Method (SNGM), the zinc oxide flowers like were prepared by direct method as follows: 50 ml of an aqueous solution (0.1 mol  $l^{-1}$ ) of zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) was prepared. 50 ml of an aqueous solution of sodium hydroxide (NaOH) (1.5 mol  $l^{-1}$ ) was also prepared. The NaOH aqueous solution was gradually added to the zinc nitrate aqueous solution. At the beginning of this process, a  $Zn(OH)_2$ precipitate was obtained. As more of the NaOH solution was added, the Zn(OH)<sub>2</sub> precipitate dissolved to yield a homogeneous clear aqueous solution containing  $Zn(OH)_4^{2-}$  ions. The aqueous solution was kept in a polypropylene beaker at 348, 358, 363 or 368 K for 3 h with a rubber stopper to prevent evaporation of the solvent. After this heating procedure, a precipitate was formed. The obtained precipitate was filtered with suction and dried at 348 K for 12 h.

The second method SNGM is a multistep synthesis of complex nanostructured films that begins with substrate preparation for heterogeneous nucleation of oriented nanocrystals, on many substrates, this can be accomplished with self-assembled monolayers (SAMs), but an even more straightforward approach is to seed the substrate with nanoparticles of the desired film material.

The decomposition or hydrolysis of zinc salts is an established route to the formation of ZnO colloids and nanocrystals in aqueous solution. We adapted this approach to form layer of ZnO nanocrystals directly on a substrate by thermally decomposing of zinc acetate at 350-400 °C. In our optimized procedure, a substrate is wet with a droplet of 0.005 M zinc acetate dehydrate (98%, Aldrich) in ethanol, rinsed with clean ethanol after 10 s, and then blown dry with a stream of argon. This coating step is repeated three to five times. The substrate, now covered with a film of zinc acetate crystallites, is heated to 350 °C in air for 20 min to yield layers of ZnO islands with their (0001) planes parallel to the substrate-independent and occurs on flat surfaces regardless of their crystallinity or surface chemistry, including ZnO single crystals. The zinc acetate deposition and decomposition procedure is carried out twice to ensure a complete and uniform coverage of ZnO seeds.

After uniformly coating the silicon wafer with ZnO nanocrystals, hydrothermal ZnO growth was carried out suspending the wafer upside-down in a opencrystallizing dish filled with an aqueous solution of zinc nitrate hydrate(0.025 M) and diethylenetriamine (0.025 M) in a in a Parr Digestion Bomb model 4748 at 363 °K. Reaction times spanned from 0.5 to 6 h. The

wafer was then removed from solution, rinsed with deionized water, and dried. We grew vertical ZnO nanowire arrays from the aligned nanocrystal seeds in an aqueous solution at 90 °C.

We have used several synthesis steps to produce oriented nanostructures that are much more complex that simple nanorod architectures and repeated sequentially the steps before mentioned and the rods were nucleated tree or four times to synthesize the ZnO "flowers like". The desired nanostructures were produced by altering the experimental conditions of DM and SNGM methods by modification of process parameters and by the chemical quality of modification and the quantity of steps in the case of SNGM method.

The zinc oxide "flowers like" also were prepared by modified direct method (MDM) as follows: 30 ml of an aqueous solution (0.1 mol  $1^{-1}$ ) of zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) was prepared. 30 ml of an aqueous solution of sodium hydroxide (NaOH) (1.5 mol  $1^{-1}$ ) was also prepared. The NaOH aqueous solution was added to the zinc nitrate aqueous solution and mixed. The aqueous solution was kept in a Parr Digestion Bomb model 4748 at 363 °K with autogen pressure. Reaction times spanned from 3 to 6 h. After this heating procedure, a precipitate was formed. The obtained precipitate was filtered with suction and dried at 348 °K for 12 h.

Modified Sequential Nucleation and Growth Method(MSNGM), in this case we carried out experiments exactly with the same several synthesis steps like SNGM, the only different thing was that after uniformly coating the silicon wafer with ZnO nanocrystals, hydrothermal ZnO growth was carried out suspending the wafer upside-down in a opencrystallizing dish filled with an aqueous solution of zinc nitrate hydrate(0.025 M) and diethylenetriamine (0.025 M) at atmospheric pressure at 363 °K, without using a Parr Digestion Bomb with autogen pressure. Reaction times spanned from 0.5 to 6 h.

The heating time dependence of the precipitated amount of zinc oxide was estimated by heating the aqueous solutions containing  $Zn(OH)_4^{2-}$  ions for a period of time between 0 and 6 h and recording the results. 10 ml of the supernatant was separated and the concentration of  $Zn^{2+}$  ion was measured by using the EDTA chelate titration method. All of the chemicals used in this preparation were reagent grade (Aldrich, U.S.A.).

The morphology of ZnO "flowers like" was studied by scanning electron microscopy (SEM) in a Hitachi S-4500 field emission SEM operating at 5 kV. For crystal structure identification we used a Phillips automated vertical scanning powder diffractometer. The spectra were obtained between 10 and 90  $2\theta$  degrees. We used X-ray photoelectron spectroscopy XPS to surface analysis of the optimized model catalyst A.

Transmission electron microscopy (TEM) and associated techniques such as energy dispersive X-ray spectroscopy (EDS), high-resolution electron microscopy (HREM), and high-angle annular dark field (HAADF) were applied to determine the subnanometer structure, chemical composition, and homogeneity of the ZnO "flowers like". For TEM analysis, the samples were sonicated in isopropanol and deposited on lacey carbon on copper grids. TEM analysis was carried out in a JEOL 2010 F microscope equipped with a Schottky-type field emission gun, an ultra-high-resolution pole piece, and a scanning-transmission (STEM), unit with a high-angle annular dark-field detector (HAADF) operating at 200 kV.

The structures and the crystalline sizes of the obtained powders were characterized by means of X-ray diffraction (XRD) (Cu-K $\alpha$ , 40 kV, 200 mA, MXP-18, Bruker AXS Co., Ltd., Kanagawa, Japan). The lattice parameters were measured by using high purity Si crystal powder (99.999%) as an internal standard. An optical system of SS = 1°, DS = 1°, RS = 0.15 mm and a graphite monochrometer was used.

In order to examine the concentration of alkali metal ion in the obtained zinc oxide precipitate, 0.1 g of the completely dried zinc oxide powder was dissolved into 10 ml of HCl aqueous solution (2 mol  $l^{-1}$ ) and the total volume of the solution was adjusted to 100 ml. The concentration of the alkali metal ion in the solution was measured by atomic absorption spectroscopy. The molar ratio of the alkali metal ion in the obtained zinc oxide was less than 0.1% in all the cases.

## **RESULTS AND DISCUSSION**

Multistep synthesis of complex nanostructured films often begins with substrate surface preparation for heterogeneous nucleation of oriented nanocrystals.

We developed seeded-growth methods that permit control over the size, population density, and spatial distribution of the ZnO crystals.

The seeds were well deposited on the substrate using many mature techniques, such as dip-/spin-coating, solgel coating, or electrophoretic deposition. In most seeding techniques, the nanoparticles are produced in a separate process before physical deposition on the substrate. However, atomic layer deposition, radiofrequency (RF) magnetron sputtering, solution coating, electrochemical deposition, and hydrothermal pretreatment produce a nanoparticle seed layer during an initial deposition step as can be seen from Figure 1 (A). Once the seed layer is formed, oriented nanocrystal growth follows in a second step (see Figure 1 (B). These two-step processes hint at the potential of using multiple reaction steps to control nanostructured-film synthesis as can be seen from Figure 1 (C), (D), (E). The synthesis of flower like by direct method can be seen in Figure 1 (F).

When nanoparticles are applied as the seeds, nanocrystal orientation and alignment could be accomplished through competition. Since the nuclei (or the seeds) are generally not well aligned on the substrate, the new crystal growth from these seeds will have no preferred



Figure 1. Synthesized Zinc Oxide (A) Seed, (B) Rods, (C) First nucleation, (D) Second nucleation, (E) Flower like sequential nucleation growth method and (F) Flower like by direct method.

orientation initially. However, as the crystals, such as nanorods, grow along the favored crystal planes, those that are not aligned normal to the substrate are soon impeded by neighboring crystals, and do not have room for further growth. Only the crystals with the growth orientation normal to the substrate can continue to grow, thus forming the oriented arrays. The size and population density of the seeds on the substrate primarily determines the size and population density of the oriented nanocrystals. ZnO nanorod arrays of highly uniform orientation were produced from epitaxial growth on <0001>-oriented seed layers.

The fundamental advantage of seeded growth is the enhanced control imparted by separating nanoparticle film nucleation and oriented rod growth into two steps. In each step, different experimental conditions can be used to optimize and control each one independently. Extending this concept, we have used several synthesis steps to produce oriented nanostructures that are much more complex than simple nanorod architectures.

#### CONCLUSION

High-quality crystallinity, orientational alignment, and high surface/volume ratios are all important for efficient electron and photon transport in applications such as photovoltaics and lasers. With ZnO, large nanorod arrays of exceptional uniformity, orientational alignment, and optical properties (negligible defect emission) have been produced by the aqueous solution route.

#### ACKNOWLEDGMENT

Authors would like to acknowledge to Facultad de Ciencias Físico Matemáticas de la Universidad Autónoma de Nuevo León, México and Professor Rick Reidy of University of North Texas at Denton for their support.

#### REFERENCES

- [1] Z. W. Pan, Z. R., Dai, Z. L. Wang, Science 291, 1947, 2001.
- [2] H. Eensmo, K. Keis, H. Lindstrom, S. Sodergren, A.Solbrand, A. Hagfeldt, S.E. Lindquist, L. N. Wang, M. Muhammed, J. Phys.Chem. B, 101, 2598, 1997.
- [3] M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, R. Russo, P. D. Yang, Science, 292, 1897, 2001.
- [4] M. Iwasaki, Y. Inubushi, S. Ito, J. Mater. Sci. Lett. 16, 1503, 1997.
- [5] Jezequel, D.; Guenot, J.; Jouini, N.; Fievet, F. J. Mater. Res. 10, 77, 1995.
- [6] O. Milosevic, D. Uskokovic, Mater. Sci. Eng. A A168, 249, 1993.
- [7] D. R. Chen, X. L. Jiao, G. Cheng, Solid State Commun. 113, 363, 2000.
- [8] C. H. Lu, Yeh, C. H. Ceram. Int. 26, 351, 2000.
- [9] T. Sekiguchi, S. Miyashita, K. Obara, T. Shishido, Sakagami, N. J. Cryst. Growth 214/215, 72, 2000.
- [10] B. Cheng and E.T. Samulski, Chem. Commun., 986, 2004.
- [11] J.M. Wang and L. Gao, J. Mater. Chem. 13, 2551, 2003.
- [12] Q.C. Li, V. Kumar, Y. Li, H.T. Zhang, T.J. Marks and R.P.H. Chang, Chem. Mater. 17, 1001, 2005.
- [13] Z. Wang, X.F. Qian, J. Yin and Z.K. Zhu, Langmuir 20, 3441, 2004.
- [14] R.A. McBride, J.M. Kelly and D.E. McCormack, J. Mater. Chem. 13, 1196, 2003.

- [15] Y. Zhang, H.B. Jia, X.H. Luo, X.H. Chen, D.P. Yu and R.M. Wang, J. Phys. Chem. B 107, 8289, 2003.
- [16] J.P. Liu, X.T. Huang, Y.Y. Li, J.X. Duan and H.H. Ai, Mater. Chem. Phys. 98, 523, 2006.
- [17] X.D. Gao, X.M. Li and W.D. Yu, J. Phys. Chem. B 109, 1155, 2005.
- [18] T. L. Breen, J. Tien, S. R. J. Oliver, T. Hadzic, and G. M. Whitesides, Science 284, 948 (1999).
- [19] R. F. Service, Science 309, 95 (2005).
- [20] J. S. Hu, Y. G. Guo, H. P. Liang, L. J. Wan, and L. Jiang, J. Am. Chem. Soc. 127, 17090 (2005).
- [21] G. M. Whitesides and M. Boncheva, Proc. Natl. Acad. Sci. USA 99, 4769 (2002).
- [22] K. Govender, D. S. Boyle, P. B. Kenway, P. O'Brien, J. Mater. Chem., 14, 2575, 2004.
- [23] W. Zhang, X. Wen, S. Yang, Inorg. Chem., 42, 5005, 2003.
- [24] W. Zhang, X. Wen, S. Yang, Y. Berta, Z. L.Wang, Adv. Mater., 15, 822, 2003.
- [25] L. Zhang, J. C. Yu, M. Mo, L. Wu, Q. Li, K. W. Kwong, J. Am. Chem. Soc., 126, 8116, 2004.
- [26] H. Hou, Y. Xie, Q. Li, Cryst. Growth Des., 5, 20, 2005.
- [27] Y. Li, Z. Wang, X.-D. Ma, X.-F. Qian, J. Yin, Z.-K. Zhu, J. Solid State Chem., 177, 4386, 2004.
- [28] S. Peulon, D. Lincot, J. Electrochem. Soc., 145, 864, 1998.
- [29] R. Konenkamp, K. Boedecker, M. C. Lux-Steiner, M. Poschenrieder, E. Zenia, C. Leavy-Clement, Appl. Phys. Lett., 77, 2575, 2000.
- [30] M. Wong, A. Berenov, X. Qi, M. Kappers, Z. Barber, B. Illy, Z. Lockman, M. Ryan, J. MacManus-Driscoll, Nanotechnology, 14, 968, 2003.
- [31] M. Izaki, T. Omi, Appl. Phys. Lett. 68, 2439, 1996.
- [32] Canava, D. Lincot, J. Appl. Electrochem., 30, 711, 2000.
- [33] R. Liu, A. A. Vertegel, E. W. Bohannan, T. A. Sorenson, J. A. Switzer, Chem. Mater., 13, 508, 2001.
- [34] R. Liu, F. Oba, E. W. Bohannan, F. Ernst, J. A. Switzer, Chem. Mater., 15, 4882, 2003.
- [35] M. J. Siegfried, K.-S. Choi, Adv. Mater. 16, 1743, 2004.
- [36] M. Maosong, J. C. Yu, L. Zhang, S.-K. A. Li, Adv. Mater., 17, 756, 2005.
- [37] Z.Wang, X.-F. Qian, J. Yin, Z.-K. Zhu, Langmuir, 20, 3441, 2004.
- [38] X. Gao, X. Li, W. Yu, J. Phys. Chem. B, 109, 1155, 2005.
- [39] A. Jackson, J. Vincent, R. Turner, Proc. R. Soc. London Ser. B, 234, 415, 1988.