

Growth of ZnO Nanoneedles by Thermal Oxidation of Metallic Zinc Microparticles in Air

Samiullah, Ajab Khan Kasi, Jafar Khan Kasi

Abstract—ZnO is multifunctional semiconductor material having useful practical applications. ZnO is promising in various scientific fields like energy harvesting, sensors, nanogenerators, optoelectronics, transducers and biomedical devices due to fascinating and remarkable properties. We report growth of ZnO nanoneedles by thermal oxidation of micro particles of metallic zinc in air at 480 °C and 500 °C. The zinc particles are deposited on the Si substrate by dip coating method. Zinc deposited substrates are oxidized by thermal radiation method in halogen tube furnace. The whole needles are wurtzite single crystal. The growth concentration and density of nanoneedles depends on the size of metallic zinc particles, oxidation time and oxidation temperature. Scanning electron microscope (SEM).

Keywords—ZnO nanoneedles, Oxidation, Halogen tube furnace.

I. Introduction

Semiconductor oxides have a series of essential application in photonics, optoelectronic devices, sensors and nanogenerators [1]. ZnO is semiconductor having direct wide band gap of 3.37 eV and large exciton energy of 60 meV at room temperature [1,2]. Nano structure of ZnO includes, Nanowires [3-5], nanoneedles [6], nanorods [7,8], nanofibers [9] and nanotubes [10] have number of applications in the field of nanotechnology. ZnO is efficient for light emitting diode (LED) [11], piezoelectric diode [12], piezoelectric nanogenerators [13], UV laser [14], field emission devices [15] and dye sensitized solar cell [16].

ZnO nano structure have been synthesized by different techniques, such as physical vapor deposition (PVD) [17], metal-organic chemical vapor deposition (MOCVD) [18], vapor liquid solid (VLS) [19], hydrothermal growth [20], molecular beam epitaxy (MBE) [7], electrospinning [21], pulsed laser deposition [8], sputtering [22], thermal evaporation [23] and oxidation of zinc [2-6].

Among these growth techniques, ZnO nanowires by thermal oxidation of zinc is very compatible with silicon based microfabrication processes [16]. Metallic zinc can be

oxidized by different method, such as oxidation of zinc in Hydrogen per oxide (H_2O_2) [6], two step oxidation [2], low temperature thermal oxidation [4], Low-temperature orientation-selective growth [24] and Wet oxidation [25].

The growth mechanism of grown ZnO nanowires due oxidation of zinc is still unclear. Much efforts has been devoted to reveal the growth behavior of ZnO nanowires. Gui et al. reported that oxidation of zinc increases the surface thickness and stress between the grain boundaries of ZnO crystals, which results into the formation of cracks and nanorods from the cracks [6]. Zhao et al. reported the formation of tiny ZnO nanowires with in the grains due to volume expansion after oxidation effects. These ZnO seeds behaves as nucleation site for the growth of ZnO nanowires when the temperature rises above than melting point of zinc (419.5 °C) [5]. They further explained the growth of ZnO nanowires on the edges of hexagonal zinc grains by thermal oxidation is due to side or surface of hexagonal zinc grain have high energy than that of bottom and top reported elsewhere [26]. The growth of nanowires also depends upon the size of zinc particle oxidation source used for the oxidation of zinc.

In tow step of oxidation of Zn nano and microparticles, for oxidation hydrogen per oxide (H_2O_2) were used as source of oxidation. The concentration of H_2O_2 played essential role in growth of ZnO nanoneedles no impurities were observed during morphological characterization. Increasing the concentration of H_2O_2 and decreasing the size of Zn particles result into the increased growth rate of nanoneedles. The author further explained the melting of Zn before oxidation arises when the content of ZnO film formed on the surface of oxidized particle is less than 50.4%. On the contrary the Zn particles initiated oxidation before the melting of Zn in the particles covered by ZnO shell [6].

In this paper, we illustration the oxidation method of zinc microparticles for the growth of ZnO nanoneedles in halogen tube furnace. The growth mechanism, oxidation rate and formation of single crystal ZnO nanoneedles are discussed. The pure metallic zinc microparticles were used as source material for oxidation. The ZnO nanoneedles are believed to be grown by mechanism of stress due to volume expansion of oxidized zinc and nanowires formation is from the cracks produced by volume expansion.

II. Experimental Procedure

A pure metallic zinc microparticles were deposited on Si (100) substrate by dip coating method. Before depiction of metallic zinc Si substrate were cleaned in acetone, alcohol and deionized water for 15 mints each. For making solution of Zn/Ethanol a 1gm of pure metallic zinc powder were pursed into the 10ml of ethanol and stirred for 45 mints at 60 °C. The Si substrate were dipped into the Zn/ethanol solution and annealed at 40 °C for 5 mints. For oxidation the

Samiullah
Department of Physics, University of Balochistan, Quetta
Pakistan

Ajab Khan Kasi
Department of Physics, University of Balochistan, Quetta
Pakistan

Jafar Khan Kasi
Department of Physics, University of Balochistan, Quetta
Pakistan

samples were put into 2cm × 10cm quartz tube placed in Halogen Tube furnace. The oxidation were carried at 500 °C for 2 hours in atmospheric air. After oxidation the samples were cooled down to the room temperature. The surface morphology of the as grown ZnO nanoneedles were examined in scanning electron microscope (SEM).

iii. Experimental Arrangement

Experimental setup for the oxidation is shown in Figure.1. The zinc microparticles Si substrate were put into the horizontal quartz tube placed in Halogen tube furnace. For oxidation at temperature above than melting point of metallic zinc quartz tube were heated in thermal radiation halogen tube furnace. The temperature controller were used to control and monitor the temperature of the furnace as shown in Figure 1.a. In furnace the quartz tube were passed in between four set of halogen tubes of 500 watt A thermocouple was inserted from one end of the quartz tube and other end the tube remained open for air entrance. Quartz tube and halogen tubes were covered by heat resistive bricks sealed in steal box shown in Figure 1.b. radiation of halogen tubes in the furnace. The temperature controller were used to control and monitor the temperature of the furnace. the halogen lamps were covered by heat resistive bricks which were salad in steal box.

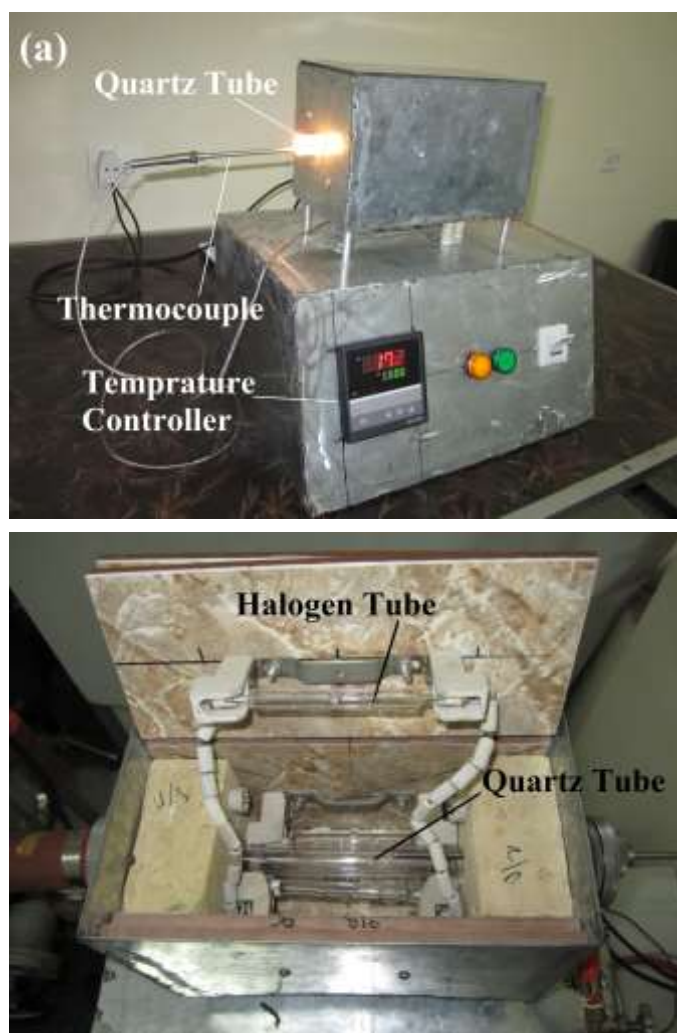


Figure 1. The camera images of the Halogen tube furnace (a) Halogen tube furnace with temperature controller during oxidation of zinc (b) Inner view of the halogen tube furnace.

iv. Results and Discussions

The SEM images of the oxidized zinc microparticles are shown in Figure.2. The zinc microparticles are in the range of 5-10µm. Figure.2.a, b shows the dense view of the oxidized microparticles with grown ZnO nanoneedles on the surface of the zinc microparticles. The grown ZnO nanoneedles by oxidation zinc microparticles with high resolution SEM image are shown in Figure.2.c. The morphology of the grown ZnO nanoneedles with thick bottom and thin at the top edges are shown in Figure.2.d.

The growth mechanism for the growth of ZnO nanoneedles was reported by Zhao et al .The zinc microparticles particles initially oxidized and forming thick oxide layer on the surface of the microparticles at low temperature (200°C). On further increasing the oxidation temperature ZnO nanoneedles are formed from the grain boundaries of the ZnO thick layer. During the oxidation of metallic zinc in air weight of ZnO increases which increases thickness of ZnO film formed on the surface of Zn microparticles. Increasing temperature of the zinc microparticles increases the thickness of the ZnO layer on surface of microparticles which reduces space between the ZnO grains. These reduced space between the grains produces stress on further increasing temperature and oxidation time tends to produce cracks on ZnO thick film. These cracks were nucleation sites for the growth of nanoneedles [5].

On the bases of above mechanism we observed that oxidation of Zn microparticles were increased by increasing temperature and oxidation time. The oxidation of Zn microparticles were initiated below 200°C and thin ZnO film were formed on the surface of microparticles and oxidation rate of inner zinc further slowdown. As the temperature were increased from 250 °C to 419.5 °C cracks appeared on the ZnO film. These cracks were due to formation thick ZnO film on further oxidation and stress between the ZnO grains by increased temperature. ZnO nanoneedles with sharp tips were observed initiated from cracks on the surface of ZnO.

It was also examined that microparticles with smaller size were having denser growth of nanoneedles with large aspect ratio as compared to large microparticles. It is because of smaller microparticles have large surface-to-volume ration and are more reactive for oxidation and on other hand large size microparticles have less energy for oxidation. Nanoneedles were grown on the surface of microparticles with larger size when the temperature were greater than melting point of Zn. As the temperature increases molten liquid Zn in core of microparticles becomes vapor and comes out from the cracks for further oxidation. Surface oxide layer becomes more and more thick and compact when the growth time is increased. The ZnO layer formed on the surface Zn particles serve as “seeds” for the nanoneedles. The zinc ions react with oxygen at the tip of ZnO nanoneedles to form further growth of prior structure.

In summary, above discussed growth mechanism of ZnO nanoneedles could be concluded as induced-stress mechanism. The formation of zinc oxide nano structure is driven by stress due to volume expansion and concentration gradients.

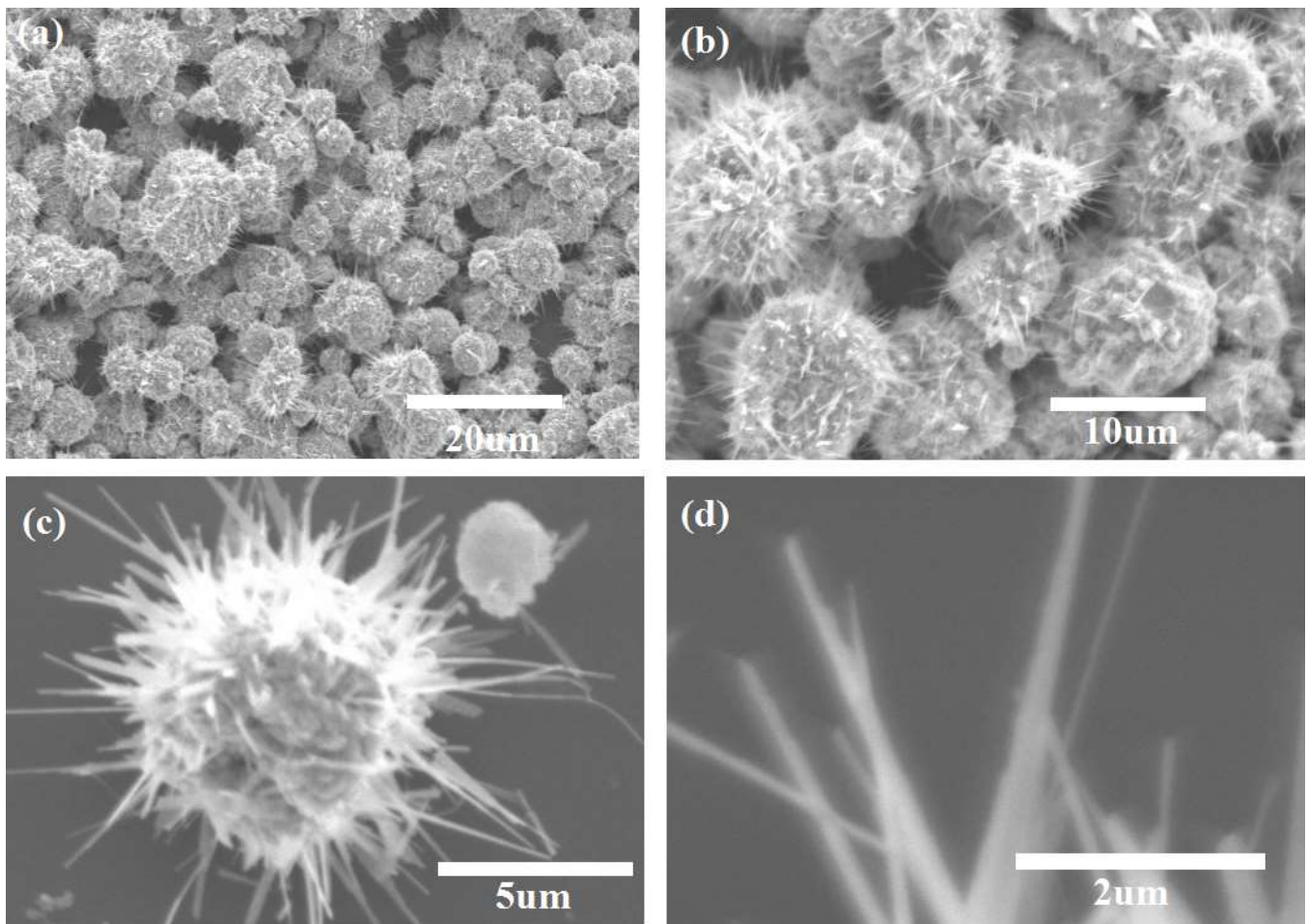


Figure 2. SEM images of ZnO nanoneedles by thermally oxidized zinc microparticles (a-d) Zinc microparticles oxidized at 480 °C for 2h (a) Oxidation at 500 °C for 2h (b) A zinc microparticle oxidized at 500 °C for 2h (c) ZnO nanoneedles after oxidation at 500 °C.

v. Conclusions

We have reported a novel method for the oxidation of zinc microparticles and growth of single crystal ZnO nanoneedles in halogen tube furnace at 500 °C for 2h. The nanoneedles growth rate can be controlled by oxidation temperature and time.

Acknowledgment

Samiullah, Ajab Khan Kasi and Jafar Khan kasi contributed to this work equally. The authors gratefully acknowledge the support of Nanotech Lab Department of Physics University of Balochistan, Quetta. The research leading to results here was fully support by research group of Physics Department.

References

- [1] Zhang, Q., Dandeneau, C. S., Zhou, X., & Cao, G. (2009). ZnO nanostructures for dye-sensitized solar cells. *Adv. Mater*, 21(41), 4087-4108.
- [2] Chen, S. J., Liu, Y. C., Ma, J. G., Zhao, D. X., Zhi, Z. Z., Lu, Y. M., ... & Fan, X. W. (2002). High-quality ZnO thin films prepared by two-step thermal oxidation of the metallic Zn. *Journal of crystal growth*, 240(3), 467-472.
- [3] Khanlary, M. R., Vahedi, V., & Reyhani, A. (2012). Synthesis and characterization of ZnO nanowires by thermal oxidation of Zn thin films at various temperatures. *molecules*, 17(5), 5021-5029.
- [4] Ren, S., Bai, Y. F., Chen, J., Deng, S. Z., Xu, N. S., Wu, Q. B., & Yang, S. (2007). Catalyst-free synthesis of ZnO nanowire arrays on

zinc substrate by low temperature thermal oxidation. *Materials letters*, 61(3), 666-670.

- [5] Zhao, C. X., Li, Y. F., Zhou, J., Li, L. Y., Deng, S. Z., Xu, N. S., & Chen, J. (2013). Large-scale synthesis of bicrystalline ZnO nanowire arrays by thermal oxidation of zinc film: growth mechanism and high-performance field emission. *Crystal Growth & Design*, 13(7), 2897-2905.
- [6] Gui, Y., & Xie, C. (2005). A novel simplified method for preparing ZnO nanoneedles via H₂O₂ pre-oxidation. *Materials Chemistry and physics*, 93(2), 539-543.
- [7] Heo, Y. W., Varadarajan, V., Kaufman, M., Kim, K., Norton, D. P., Ren, F., & Fleming, P. H. (2002). Site-specific growth of ZnO nanorods using catalysis-driven molecular-beam epitaxy. *Applied physics letters*, 81(16), 3046-3048.
- [8] Okada, T., Aemura, B. H., & Nakata, Y. (2004). ZnO nano-rods synthesized by nano-particle-assisted pulsed-laser deposition. *Applied Physics A*, 79(4-6), 1417-1419.
- [9] Wu, H., & Pan, W. (2006). Preparation of zinc oxide nanofibers by electrospinning. *Journal of the American Ceramic Society*, 89(2), 699-701.
- [10] Hu, J. Q., Li, Q., Meng, X. M., Lee, C. S., & Lee, S. T. (2003). Thermal reduction route to the fabrication of coaxial Zn/ZnO nanocables and ZnO nanotubes. *Chemistry of materials*, 15(1), 305-308.
- [11] Gao, H., Yan, F., Li, J., Zeng, Y., & Wang, J. (2007). Synthesis and characterization of ZnO nanorods and nanoflowers grown on GaN-based LED epitaxial wafer using a solution deposition method. *Journal of Physics D: Applied Physics*, 40(12), 3654. (LED)
- [12] Yang, Q., Wang, W., Xu, S., & Wang, Z. L. (2011). Enhancing light emission of ZnO microwire-based diodes by piezo-phototronic effect. *Nano letters*, 11(9), 4012-4017.
- [13] Wang, Z. L., & Song, J. (2006). Piezoelectric nanogenerators based on zinc oxide nanowire arrays. *Science*, 312(5771), 242-246. (nanogenerator)

- [14] Huang, M. H., Mao, S., Feick, H., Yan, H., Wu, Y., Kind, H., ... & Yang, P. (2001). Room-temperature ultraviolet nanowire nanolasers. *science*, 292(5523), 1897-1899. (UV LASER)
- [15] Zhu, Y. W., Zhang, H. Z., Sun, X. C., Feng, S. Q., Xu, J., Zhao, Q., ... & Yu, D. P. (2003). Efficient field emission from ZnO nanoneedle arrays. *Applied Physics Letters*, 83(1), 144-146.
- [16] Hue, H., Bader, M., Mair, P., & Glatzel, T. (2014). Bionphotovoltaics: natural pigments in dye-sensitized solar cells. *Applied Energy*, 115, 216-225.
- [17] Tisli, O., & Juhala, J. (2011, August). ZnO nanowire growth by physical vapor deposition. In *Nanotechnology (IEEE-NANO), 2011 11th IEEE Conference on* (pp. 608-611). IEEE.
- [18] Lee, W., Jeong, M. C., & Myoung, J. M. (2004). Catalyst-free growth of ZnO nanowires by metal-organic chemical vapour deposition (MOCVD) and thermal evaporation. *Acta Materialia*, 52(13), 3949-3957.
- [19] Huang, M. H., Wu, Y., Feick, H., Tran, N., Weber, E., & Yang, P. (2001). Catalytic growth of zinc oxide nanowires by vapor transport. *Advanced Materials*, 13(2), 113-116.
- [20] Kang, D. S., Lee, H. S., Han, S. K., Srivastava, V., Babu, E. S., Hong, S. K., ... & Kim, D. (2011). Growth and optical properties of ZnO nanorods prepared through hydrothermal growth followed by chemical vapor deposition. *Journal of Alloys and Compounds*, 509(16), 5137-5141.
- [21] Sui, X. M., Shao, C. L., & Liu, Y. C. (2005). White-light emission of polyvinyl alcohol/ZnO hybrid nanofibers prepared by electrospinning. *Applied Physics Letters*, 87(11), 113115.
- [22] Chiou, W. T., Wu, W. Y., & Ting, J. M. (2003). Growth of single crystal ZnO nanowires using sputter deposition. *Diamond and Related Materials*, 12(10), 1841-1844.
- [23] Yao, B. D., Chan, Y. F., & Wang, N. (2002). Formation of ZnO nanostructures by a simple way of thermal evaporation. *Applied Physics Letters*, 81(4), 757-759.
- [24] Kim, T. W., Kawazoe, T., Yamazaki, S., Ohtsu, M., & Sekiguchi, T. (2004). Low-temperature orientation-selective growth and ultraviolet emission of single-crystal ZnO nanowires. *Applied physics letters*, 84(17), 3358-3360.
- [25] Chen, R. Q., Zou, C. W., Yan, X. D., & Wei, G. A. O. (2011). Zinc oxide nanostructures and porous films produced by oxidation of zinc precursors in wet-oxygen atmosphere. *Progress in Natural Science: Materials International*, 21(2), 81-96.
- [26] Kong, X. Y.; Wang, Z. L. *Nano Lett.* 2003, 3, 1625-1631. (Kong, X. Y., & Wang, Z. L. (2003). Spontaneous polarization-induced nanohelices, nanosprings, and nanorings of piezoelectric nanobelts. *Nano Letters*, 3(12), 1625-1631.)



Samiullah received his M.Sc degree in Physics from University of Balochistan, Quetta. He is doing M.Phil from University of Balochistan, Quetta. He is currently working as Lecturer in department of Physics, University of Balochistan, Quetta. His research area is energy harvesting based upon ZnO nanoballoons solar cell, advance materials, nanostructure and its applications. .