

---

---

# INFLUENCE OF SYNTHESIS CONDITIONS ON ZINC OXIDE NANORODE LAYER MORPHOLOGY\*

---

---

Konrad DUNST<sup>†</sup>, Jakub KARCZEWSKI<sup>‡</sup>, Piotr JASINSKI<sup>§</sup>

---

**Keywords:** zinc oxide; nanorods; chemical bath deposition

**Abstract:** In recent years one dimensional (1D) nanostructures (nanotubes, nanowires, nanoribbons and nanorods) have been widely studied. Among studied nano-materials, the greatest interest can be seen for zinc oxide (ZnO). However, there is still a need for simple, inexpensive and reproducible fabrication method.

In the literature different fabrication methods can be found, most of them requires expensive equipment and involve complex fabrication process. An alternative is chemical bath deposition (CBD). This method is simpler than the others and does not require sophisticated equipment.

In this paper the CBD method is studied for fabrication of ZnO nanorods. The influence of synthesis temperature and time are studied. Relation between these conditions and ZnO morphology are showed. The length and diameter of ZnO nanorods are taken under consideration. Typically, the synthesized ZnO nanorods are 100-300 nm in diameter and 0.8-4  $\mu\text{m}$  long.

---

## 1. Introduction

Zinc oxide (ZnO) attracted interest in recent years due to its properties. The most important of them are wide band gap of 3.37 eV, large exciton binding energy of 60 meV, stable physical and chemical properties (Wang et al., 2009). Zinc oxide is widely used in solar cells, sensors, field effect transistors, light emitting diodes and others. Development in the zinc oxide area recently moving towards nanostructures. The most promising of them are one dimensional (1-D) nanostructures such as nanotubes, nanoribbons (Yao et al., 2002), nanowires (Huang et al., 2001), nanobelts (Pan et al., 2001), nanocables and nanorods (Yang et al., 2009). The greatest problem

---

\*This work was supported by the National Centre for Research and Development, project LIDER No. 22/103/L-2/10/NCBiR/2011 "Multisensor system for measuring air pollutants".

<sup>†</sup>Faculty of Electronics, Telecommunications and Informatics, Department of Biomedical Engineering, Gdansk University of Technology

<sup>‡</sup>Faculty of Applied Physics and Mathematics, Department of Solid State Physics, Gdansk University of Technology

<sup>§</sup>Faculty of Electronics, Telecommunications and Informatics, Department of Biomedical Engineering, Gdansk University of Technology



is the fabrication process. Until now, many techniques were used to synthesize 1-D nanostructures, such as pulse laser deposition (Sun et al., 2004), chemical vapour deposition (Park et al., 2002) and electrochemical deposition (Yu et al., 2005). All of them need sophisticated and expensive equipment, require complex process and high temperatures. Chemical bath deposition (CBD) (Abbasi et al., 2012) in comparison to the other methods is much simpler. It requires low temperature (around 90°C) and a vessel with a starting solution. The biggest drawback of that method is lack of repeatability. Furthermore, orientation and size is hard to control.

In the literature CBD method most frequently occurs as a two-step process. First step is the application of the seed layer. Many methods were used to fabricate that layer, among them a thermal deposition (Tak and Yong, 2005), a radio frequency magnetron sputtering and a spin coating (Xinjian et al., 2004) were the most often used. Second step is the main CBD process when the main layer is produced.

In this paper a two-step chemical bath deposition was studied as an effective way to produce ZnO nanorods layers. As a seed layer nanoparticles of zinc oxide were used and fabricated by spin coating. Influence of temperature and reaction time were studied. Nanorods diameter and length were investigated.

## 2. Experimental

All chemicals were purchased from Sigma Aldrich. Zinc oxide nanorods layers were prepared by two-step method consisting of seed layer deposition and nanorods layer growing. Firstly, a suspension of nano-ZnO was prepared by method presented by Schwartz et al. (2003). Briefly, tetramethylammonium hydroxide (2.5 mmol) was dissolved in ethanol (5 ml) and added drop-wise to a solution of zinc acetate dihydrate (0.1 M) in dimethylsulfoxide (15 ml) under vigorous stirring at room temperature. After 24 hours ZnO nanocrystals were washed by precipitation with ethylacetate. Obtained in this way ZnO nanoparticles were re-suspended in ethanol and spin coated (Laurell WS-400A-6NPP/LITE, 4000 rpm, 1 min) on glass substrate. Before spin coating glass substrates were cleaned ultrasonically in acetone and isopropyl alcohol and rinsed with deionized water. The spin coating process was repeated 4 times, after each deposition, the substrate was annealed at 400°C for 30 minutes. Resulting layer was characterized by atomic force microscopy (Nanosurf Easy Sacn 2) – the average crystallite sizes were 100 nm.

Zinc oxide nanorods were deposited by chemical batch deposition. The seeded substrates were placed horizontally in autoclavable flask filled with solution of 0.1 M zinc nitrate and 0.1 M hexamethylenetetramine (Abbasi et al., 2012). The flask was placed into the muffle furnace and heated to the desired temperature. Four temperatures, 70°C, 90°C, 110°C and 120°C, were studied. The heating time was varied from 1 hour to 6 hours. After annealing the substrate were rinsed with deionized water and dried. Morphology of the resulting layer was studied by the scanning electron microscopy (FEI QUANTA FEG 250, 10<sup>-4</sup> Pa, 30 kV).



### 3. Results and Discussion

#### 3.1. Influence of time

In order to investigate the effect of reaction time on morphology, four deposition times were selected. Namely, the layers were deposited for 1, 2, 4 and 6 hours at the same temperature of 90°C. This temperature was chosen because of its frequent occurrence in the literature. The fabricated layers were examined by SEM microscopy. Every synthesized nanorod structure was in the cross-section in the shape of a hexagon. This structure is mostly obtained for CBD method (Abbasi et al., 2012). The SEM images of the film cross-sections are presented in Fig. 1, where the produced layers could be easily seen. During observations the denser layer was noticed on the side closer to the glass substrate. Most likely, it is originated from the seed layer. The presence of the dense layer could be a significant factor for electronic applications. The dense layer improves conductivity of the film. However, it may overshadow the properties of the nanorods.

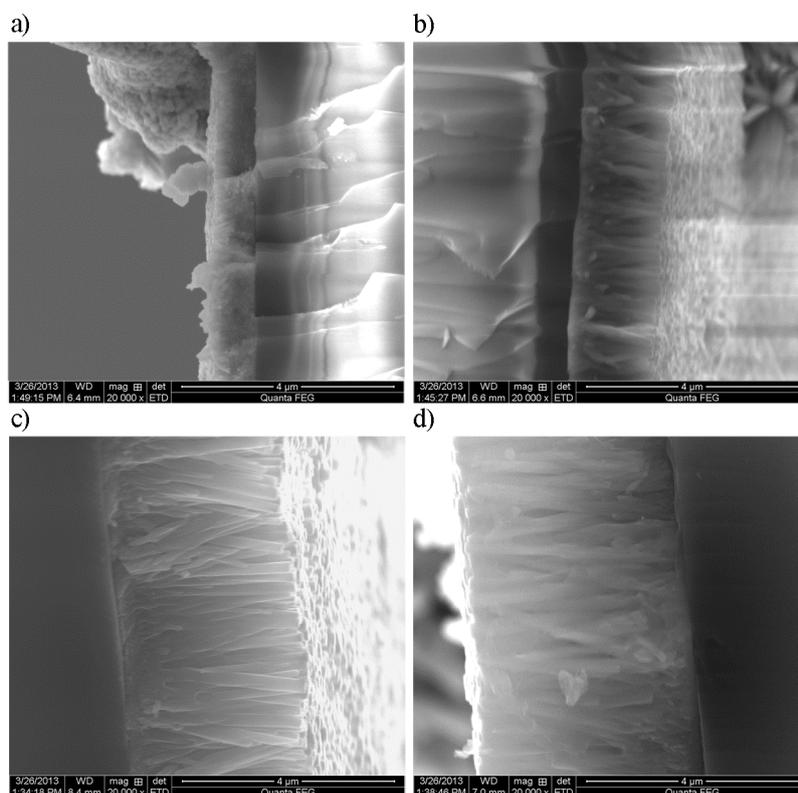


Fig. 1. Cross-section SEM images of the ZnO layer fabricated at temperature of 90°C and time a) 1h, b) 2h, c) 4h and d) 6h



In Tab. 1 the relation between the deposition time and the average diameter of nanorod is presented. With increasing temperature, the diameter increase. The maximum diameter for the synthesis time of 4 hours (242 nm) was obtained. Most probably, with the CBD method and with this seed layer, it was not possible to fabricate thicker nanorods. The minimum diameter of nanorod was limited by the size of seed layer particles (100 nm).

Tab. 1. Diameter of ZnO nanorods fabricated at 90°C for different synthesis time

time [h]	1	2	4	6
diameter [nm]	106	140	242	242

The relation between the layers thickness and synthesis time is presented in Fig. 2. This relation is nearly linear. From the slope of the plot the layer formation speed was determined. For the whole layer the speed was 11.2 nm per minute, while for dense layer 3.6 nm per minute. The most homogenous layer, by the cross-section and surface criteria, was layer fabricated during deposition time of 4 hours. For further studies that synthesis time were used.

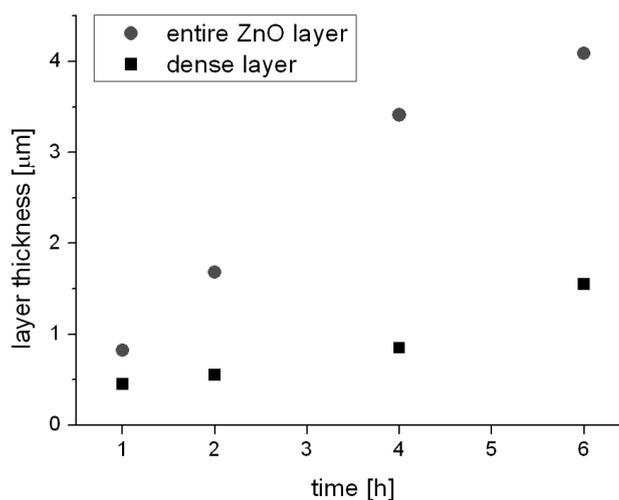


Fig. 2. Layers thickness as a function of synthesis time

### 3.2. Influence of temperature

To investigate the influence of deposition temperature the following were used: 70°C, 90°C, 110°C and 120°C. The synthesis was carried for 4 hours. Surfaces of the layers were presented at Fig. 3. At lower temperature (70°C) almost all nanorods were connected and low porosity was observed. At high temperatures (110-120°C) rods were also connected but porosity were higher than that observed for sample prepared



at temperature of 70°C. The structure of rods fabricated at higher temperature was not always hexagons. Pentagons and expanded hexagons were also observed. Unfortunately, it was not possible to perform cross-sections of these layers. The average diameters (Tab. 2) were almost the same for all studied samples. Decrease of diameter is noticeable at the temperatures of 70°C and 120°C.

Tab. 2. Diameter of ZnO nanorods fabricated at different temperatures for 4 hours

temperature [°C]	70	90	110	120
diameter [nm]	210	242	225	207

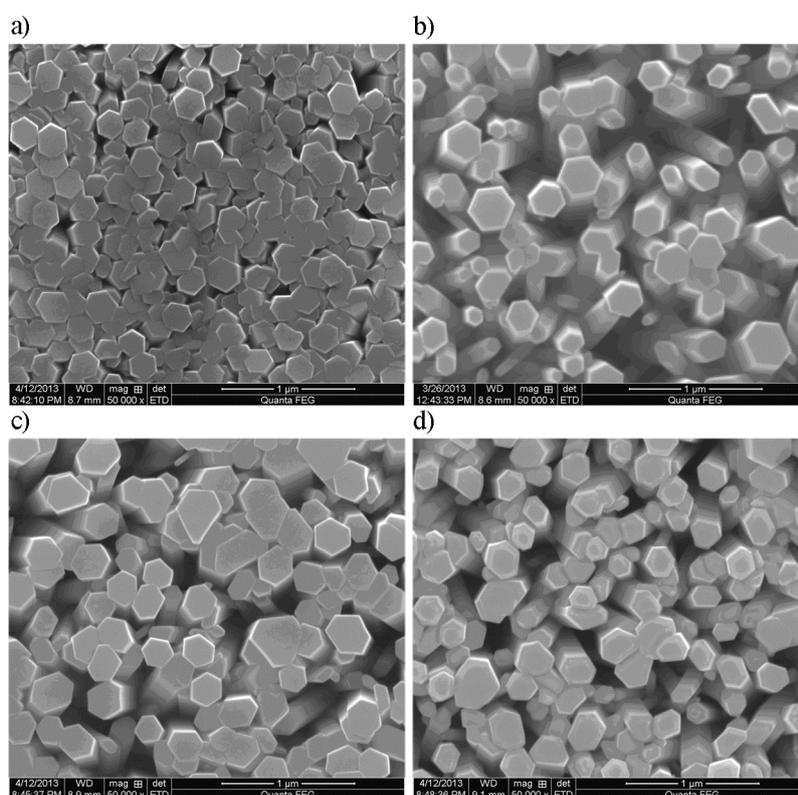


Fig. 3. Surface of the ZnO layer fabricated at temperatures of a) 70°C, b) 90°C, c) 110°C and d) 120°C for 4 hours



#### 4. Conclusion

Chemical bath deposition was studied as an alternative way for fabrication of uniform ZnO layers. This method allowed obtaining homogeneous layers of zinc oxide nanorods. The relation between diameter and reaction parameters was studied. As time increases the diameter became bigger (up to 242 nm). The temperature of synthesis had influence on the morphology of the film surface. When temperature was too low or too high, the ZnO rods were connected and less porous structures were fabricated. The relation between layer thickness and synthesis time was obtained. Additional dense layer in the film was noticed, what could affect the electrical properties. All produced layers were sufficiently well orientated. The shape of nanorods was always hexagonal at reaction temperature of 90°C. For further investigation it is crucial to take into account seed layer morphology. It is also necessary to carry out test of repeatability.

#### References

- Abbasi, M. A., Y. Khan, S. Hussain, O. Nur and M. Willander (2012), 'Anions effect on the low temperature growth of zno nanostructures', *Vacuum* **86**(12), 1998 – 2001.
- Huang, M. H., S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo and P. Yang (2001), 'Room-temperature ultraviolet nanowire nanolasers', *Science* **292**(5523), 1897–1899.
- Pan, Z. W., Z. R. Dai and Z. L. Wang (2001), 'Nanobelts of semiconducting oxides', *Science* **291**(5510), 1947–1949.
- Park, W. I., D. H. Kim, S. W. Jung and G. Ch. Yi (2002), 'Metalorganic vapor-phase epitaxial growth of vertically well-aligned zno nanorods', *Applied Physics Letters* **80**(22), 4232–4234.
- Schwartz, D. A., N. S. Norberg, Q. P. Nguyen, J. M. Parker and D. R. Gamelin (2003), 'Magnetic quantum dots: Synthesis, spectroscopy, and magnetism of co<sup>2+</sup>- and ni<sup>2+</sup>-doped zno nanocrystals', *Journal of the American Chemical Society* **125**(43), 13205–13218.
- Sun, Y., G. M. Fuge and M. N. R. Ashfold (2004), 'Growth of aligned zno nanorod arrays by catalyst-free pulsed laser deposition methods', *Chemical Physics Letters* **396**(1–3), 21 – 26.
- Tak, Y. and K. Yong (2005), 'Controlled growth of well-aligned zno nanorod array using a novel solution method', *The Journal of Physical Chemistry B* **109**(41), 19263–19269.
- Wang, S. F., T. Y. Tseng, Y. R. Wang, Ch. Y. Wang and H. Ch. Lu (2009), 'Effect of zno seed layers on the solution chemical growth of zno nanorod arrays', *Ceramics International* **35**(3), 1255 – 1260.
- Xinjian, F., F. Lin, J. Meihua, Z. Jin, J. Lei and Z. Daoben (2004), 'Reversible super-hydrophobicity to super-hydrophilicity transition of aligned zno nanorod films', *Journal of the American Chemical Society* **126**(1), 62–63.
- Yang, L. L., Q. X. Zhao, M. Willander and J. H. Yang (2009), 'Effective way to control the size of well-aligned zno nanorod arrays with two-step chemical bath deposition', *Journal of Crystal Growth* **311**(4), 1046 – 1050.
- Yao, B. D., Y. F. Chan and N. Wang (2002), 'Formation of zno nanostructures by a simple way of thermal evaporation', *Applied Physics Letters* **81**(4), 757–759.
- Yu, H., Z. Zhang, M. Han, X. Hao and F. Zhu (2005), 'A general low-temperature route for large-scale fabrication of highly oriented zno nanorod/nanotube arrays', *Journal of the American Chemical Society* **127**(8), 2378–2379.