# Effect of nitrogen on morphology of ZnO nanorods deposited by CVD method

## L N Wang[1,2], J Wang[1], D Zhou[1], N Liu[1], J T Liu[1] and Z H Gao[1]

[1]Key Laboratory of Marine Biophysics of Liaoning Province, Dalian Ocean University, Dalian, China

E-mail: l.n.w@163.com

**Abstract.** The ZnO nanorods are synthesized by a typical CVD method without any catalyze and substrate. The concentration of nitrogen is changed by a digital gas control system. The influence on the morphology is studied in detail. Under lower amounts of nitrogen the diameter of nanorod is smaller than in the higher one. Meanwhile, the size of the nanorod is bigger in the rich nitrogen amounts. The morphology of the sample is carry out by SEM, and the crystal structure information is giving by XRD. All the measurement told that the nanorods have a great hexagonal wurtzite structure.

## 1. Introduction

As an excellent semiconductor photoelectric material Zinc oxide (ZnO) can be widely used in many areas, especially in photodetectors [1], light-emitting diode (LED) [2,3], nanogenerators [4,5] and gas sensors [6-8]. With the development of economic society, the photoelectric devices need to be more and smaller, so that the ZnO nanostructures are more useful. After many years of hard work, different morphology of ZnO nanostructure has been made, such as nanowires, nanorods, nanoflowers, nanostars and nanoflakes [9-13]. Among them ZnO nanorods exhibit more advantage, for instance the large surface-to-volume and prefer orientation. During the study process there are also some difficulties need to be overcome, the nanorods have not realized controlling deposition, because it is very sensitive to the experiment condition, such as pressure, gas concentration, deposition temperature, and it may also some other factors which has not been consider. So it is very necessary to discuss the major factor which can affect the morphology of the nanorod. The experiment technique is also a important factor, many methods have been made to deposited ZnO nanostructures, for example aqueous based chemical deposition [14], hydrothermal method [15], thermal evaporation technique [16], electrochemical solution [17], and chemical vapor deposition (CVD) [18]. Among all the methods, CVD technique exhibit is more stable, reproducible and easily to change the experiment parameter.

In this paper, we deposited ZnO nanorods using three different nitrogen concentrations without any substrate, the concentration of nitrogen are 20 sccm, 25 sccm, 30 sccm, respectively. During the whole deposition process, the nitrogen is act as carrier gas. It was found that at different concentration the ZnO exhibit different nanostructures. The mechanism of different morphology was studied in detail.

## 2. Experiment

The ZnO nanorods were deposited by CVD method without any substrate. The CVD system is composed of three parts: gas controller operation, three heating zone quartz tube furnace and

integrated digital control system. The quartz tube furnace was 120cm in length and 8cm in diameter. The melting point of ZnO is about 1975℃, in order to reduce the growth temperature,  A mix powder of ZnO 8g and graphite 2g are grinding in agate mortars, the mix powder react readily to produce Zn and $CO_2$, the melting point of Zn is about 419℃, in the next step the Zn and $O_2$ react to produce ZnO. Then the mix powder was put into one end of a small quartz tube (30 cm in length, 4 cm in diameter). The small tube is located at the central of the heating zone. The nitrogen is introduce into the system with a constant flow rate of 20 sccm(sample a), after a few minutes the impurity gas was all exhaust, turn on the digital control system to start the deposition, the deposition temperature was 1000℃, when the grow up temperature up to 800℃, introduced the oxygen with constant flow rate of 20 sccm which was act as react gas, the whole grow up process maintained 60 minutes, then the temperature cooled down to room temperature, and the ZnO nanorods can be found at another end of the small tube. Changing the flow rate of nitrogen to 25 sccm (sample b) and 30 sccm (sample c), other parameters remain the same one, the other two samples can also be found.

The morphology of the ZnO nanorods was observed in a hitachi SU1510 scanning electron microscope (SEM) system which operating at 15 KV. The structural properties detail was given by X-ray diffraction (XRD; RigakuD/max3B) which performed in a θ-2θ configuration.

## 3.  Results and discussion

The surface images of ZnO nanorods were shown in figure 1, the sample a,b,c were deposited in nitrogen under a constant flow rate of 20, 25 and 30 sccm severally. In figure 1, a it can be clearly found that the nanorods was short, and the most longest one was about 2.33 μm. There are also some nanotetrapod structure exist in the sample, the nanorods were grow up out of order and there remain some small holes exist. The nanorods have clearly hexagonal wurtzite structure with smooth surface. When the concentration of nitrogen up to 25 sccm, the morphology was clearly changed, the nanorods become more longer with smooth surface, the longest one was about 3.67 μm, meanwhile, the hollows were become bigger which means the density was decrease. In the other hand, there are few nanowires emerged in the picture. The nanorods still have a perfect hexagonal wurtzite structure. With the flow rate continue to grow, the morphology have a great change. As can be seen the nanorods gets more tall and fat, it can up to 10 μm in length, in the same time the structure also have some difference. Two different surface morphologies appeared in the same time, one is the hexagonal wurtzite structure, the other one is the hexagonal pyramids like nanorods, there are also some nanowires can be found around.
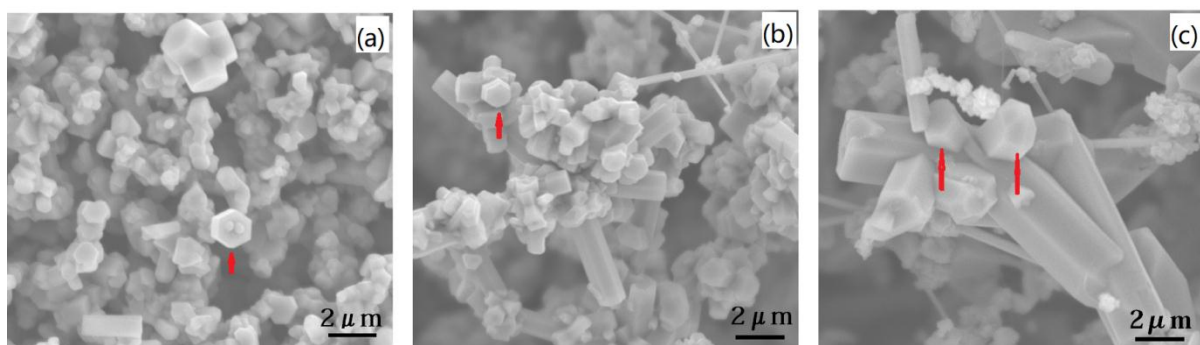


**Figure 1.** SEM images of ZnO nanorods with different amounts of nitrogen (a) 20 sccm, (b) 25 sccm and (c) 30 sccm.

From the SEM image we can see that when the flow rate increased, the nanorods became bigger and fatter. The different structures maybe explained by different mechanism. At the first stage, the carrier gas was not enough, so the process was carry on slowly, ZnO powder in the react mix source are reduced to Zn or its suboxide, due to the lowly flow rate of nitrogen the concentration of oxygen is relative bigger, as a result a lot of ZnO nuclei are formed at the low temperature area which lead to

small ZnO nanorods and nanotetrapod structures as sample a. When the flow rate up to 25 sccm, the carrier gas was increase in the same time the concentration of oxygen is decrease which lead to few ZnO nuclei, so the nanorods became a little bigger. However for the case of sample c, it is deposited under rich carrier gas atmosphere, the pressure was change a lot which result in the nanorods get bigger and fatter. It can be deduce that the pyramids-like nanorods also a result of the higher flow rate. When the concentration changed the pressure also changed which lead to a different crystal and size [19].
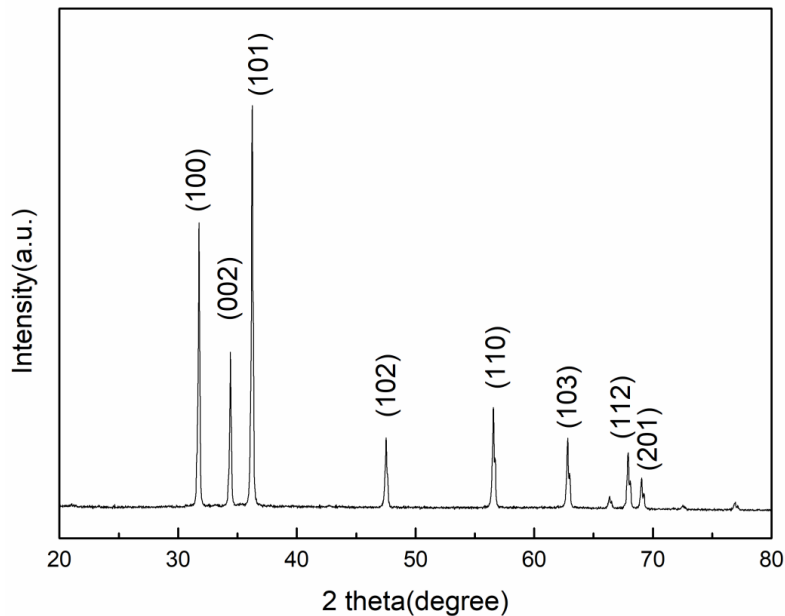


**Figure 2.** The XRD pattern of ZnO nanorods.

The XRD pattern of ZnO nanorods is shown in figure 2. The XRD test is made in this way; we put the three samples together in a small box and then using θ-2θ scanning. There are eight peaks arrives at 31.74°, 34.42°, 36.25°, 47.43°, 56.45°, 62.80°, 67.95° and 69.03° respectively which corresponding to ZnO(100), (002), (101), (102), (110), (103), (112) and (201) peaks [20]. All these peaks are related to the typical hexagonal wurtzite structure. These peaks all have a great intense especially the (101) peak which means the ZnO nanorods are in a good crystal quality. The lattice constant can be calculated as follows [21]:

$$a = \frac{\lambda}{2\sin\theta}\left(\frac{4}{3}\left(h^2 + hk + k^2\right) + \left(\frac{al}{c}\right)^2\right)^{\frac{1}{2}} \qquad (1)$$

$$c = \frac{\lambda}{2\sin\theta}\left(\frac{4}{3}\frac{\left(h^2 + hk + k^2\right)c^2}{a^2} + l^2\right)^{\frac{1}{2}} \qquad (2)$$

The (hkl) represent Miller indices, λ=0.15418 nm, θ is the diffraction angle, a and c are the lattice constant, according to equation above, the constant of the most intense (101) peak can be calculated with a=3.265 Å, c=5.214 Å. According to literature (JCPDS NO.36-451), when the ZnO exhibit hexagonal wurtzite structure, the lattice constant are a=3.427 Å, c=5.200 Å. The XRD pattern has a

great agreement with the literature which means the nanorods is grown up with hexagonal wurtzite structure.

## 4. Conclusion

In summary, the ZnO nanorods are synthesized by a simple CVD method without any substrate. By controlling the flow rate of nitrogen, the ZnO nanorods realized controlling synthesis. When the concentration of nitrogen is not enough, the diameter of the nanorods is small, there are also some small hollow exist, when the amounts of the gas carrier increasing, the nanorods become longer and bigger, there are also some nanowires emerged. In a rich nitrogen condition the diameter and length of the nanorods all increase to some extent. It can be deduced that the concentration of nitrogen can affect the pressure of the growing environment, under a rich gas condition the nanorods are long, and otherwise the nanorods are too short. The SEM and XRD all give the information that the nanorods have a great hexagonal wurtzite structure with lattice constant a=3.265 Å, c=5.214 Å.

**References**
[1]    Liang S, Sheng H, Liu Y, Huo Z, Lu Y and Shen H 2001 *J. Cryst. Growth* **225** 110-3
[2]    Tsukazaki A, Ohtomo A, Onuma T, Ohtani M, Makino T, Sumiya M, Ohtani K, Chichibu S, Fuke S, Segawa Y, Ohno H, Koinuma H and Kawasaki M 2004 *Nat. Mater.* **4** 42-6
[3]    Tsukazaki A, Kubota M, Ohtomo A, Onuma T, Ohtani K, Ohno H, Chichibu S.F and Kawasaki M 2005 *Japan J. Appl. Phys. Part 2* **44** 643-5
[4]    Yin B, Qiu Y, Zhang H, Ji J and Hu L 2014 *Cryst. Eng. Comm* **16** 6831-5
[5]    Yin B, Qiu Y, Zhang H, Ji J and Lei J 2015 *J. Mater. Sci: Mater Electron* **26** 742-6
[6]    Chen Y, Xu P C, Xu T, Zheng D and Li X X 2017 *Sens. Actuators B* **240** 264-7
[7]    Zou A L, Qiu Y, Yu J J, Yin B, Cao G Y, Zhang H Q and Hu L Z 2016 *Sens. Actuators B* **227** 65-72
[8]    Zou A L, Hu L Z, Qiu Y, Cao G Y, Yu J J, Wang L N, Zhang H Q, Yin B and Xu L L 2015 *J. Mater. Sci: Mater Electron* **26** 4908-12
[9]    Mosquera E, Bernal J, Zarate R, Mendoza F, Katiyar R and Morell G 2013 *Mater. Lett.* **93** 326-9
[10]   Zhang S, Yan C L, Zhang H X and Lu G Y 2015 *Mater. Lett.* **148** 1-4
[11]   Liu C, Wang B Q, Liu T, Sun P, Gao Y, Liu F M and Lu GY 2016 *Sens. Actuators B* **235** 294-7
[12]   Aladpoosh R and Montazer M 2016 *Carbohydr. Polym.* **141** 116-25
[13]   Behera B and Chandra S 2016 *Sens. Actuators B* **229** 414-24
[14]   Panigrahy B, Aslam M and Bahadur D 2010 *J. Phys. Chem. C* **114** 11758-63
[15]   Yoo R, Cho S, Song M J and Lee W 2015 *Sens. Actuators B* **221** 217-23
[16]   Fan D H, Zhang R and Li Y 2010 *Solid State Commun.* **150** 1911-4
[17]   Liang J K, Su H L, Kuo C L, Kao S P and Cui J W 2014 *Electrochim Acta* **125** 124-32
[18]   Ding M, Yao B, Zhao D, Fang F and Shen D 2010 *Thin Solid Films*. **518** 4390-3
[19]   Mongia H, Samir F, Frederic S, Farah K, Noureddine J, Bruno V and Arbi M 2014 *J. Alloys Compd.* **615** s472-5
[20]   Gayen R N and Paul R 2016 *Thin Solid Films* **605** 248-56
[21]   Moulahi A and Sediri F 2016 *Optik* **127** 7586-93