The growth mechanism of zinc oxide micro-rods via vapor-phase method

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Abstract. Two different ZnO micro-structures were deposited by a Chemical Vapour Deposited method in a small quartz tube. The micro-rods and micro-wires were found on the edge of the tube respectively. The morphology and structural properties were tested by scanning electronic microscopy technique and X-ray diffraction. The results shows that the micro-rods have typical hexagonal wurtzite structure without any defect and the micro-wires have two types, the single ZnO crystal and the double-like one. The X-ray diffraction gives some information through the intense 002 peak which means the samples have a great wurtzite structure and grown up along the c-axis. The mechanism of the two samples also discussed, it is in relation to the substrate temperature and the concentration of the mixed gas.

1. Introduction
Regarding as a excellent semiconductor material Zinc oxide (ZnO) could be widely used in many fields, such as gas sensors [1,2], light emitting diodes [3-5], nano generator [6-8], bioimaging application [9], optoelectronic devices [10] and so on. The ZnO could be made in two forms, one is film and the other is nanostructure. Compared with ZnO film, the superiority of ZnO nanostructure is more obvious in preparation of microelectronic devices. The controlling deposition of the nanostructure is more important to increase the photovoltaic properties. The technique to synthesis ZnO nanostructures and the growth mechanism are related to the realization of ZnO controlling deposition. There have been several kinds of nanostructures to be deposited, such as nanowires, nanorods, nanotubes, nanoplates and so on [11-17]. There are also different kinds of methods to fabricated ZnO nanostructures, the most effective way such as chemical vapour deposition methods (CVD)[18], metal-organic chemical vapor depositions [19], electrochemistry depositions [20], epitaxial electrodeposition [21], electron beam lithography [22],solution-grown methods [23]. In these methods, the CVD technique have more advantage, for example non-pollution, repeatable, stable and cost-effective. The nanowires and nanorods have bigger specific surface area which can also realize controlling deposition. All of this makes the ZnO nanowires and nanorods which deposited by CVD to be the first choice to synthesis microelectronic devices.

In our work, the ZnO micro-rods and micro-wires were deposited via a simple CVD technique. After deposition, two samples were founded at the downstream of the reaction source. The ZnO micro-rods has perfect hexagonal wurtzite structure, a small part of the nanorods exhibit cone-shape. The micro-wires has smooth surface without any attachment, the nanowires were out of order and did not perform a typical hexagonal structure. The scanning electronic microscopy (SEM) technique was introduced to examine the morphology of the samples, and the X-ray diffraction was used to test the structure properties. The mechanism of the ZnO nanostructures were also discussed in detail.
2. Experiment
The ZnO micro-rods and micro-wires were deposited by CVD technique. The CVD system was composed of four parts. The gas supply system, digital control system, horizontal tube furnace and the tail gas treatment system. The whole deposited process can be described as follows: two kinds of powder that composed of ZnO and carbon were mixed together after fully grind with mass ratio 4:1. Then the mixed powder was put into a quartz tube which is 30cm in length and 4cm in diameter. After remove all the impurity gas, the quartz tube was put into the CVD system that near the heating zone, the illustration system was shown in Figure 1. Then the nitrogen was introduced into the whole system with the flow rate of 50 standard cubic centimeter per minute (SCCM). The growth temperature was set up at 950℃, and the growth was last for 60 min. When the growth temperature up to 800℃, the oxygen was introduce into the system with a flow rate of 20 SCCM. After deposition, cut off the oxygen current, but the nitrogen was still be switch on until the whole system chill down to room temperature. After all of this, the ZnO microrods was found at the edge of the quartz tube. There are two main nanostructures can be found, the bottom one which marked as sample a is composed of micro-rods, and the upper one which marked as sample b is composed of micro-wires. The structure of the two samples were analyzed by scanning electron microscope (SEM), and X-ray diffraction (XRD).

![Diagram of experiment system](image)

**Figure 1.** The illustration of experiment system.

3. Results and discussion
The surface features of the samples were studied by SEM which were shown in Figure 2. The Figure 2a and c are corresponding to sample a in different scales, Figure 2b and d are corresponding to sample b in different scales, too. It could be clearly seen that sample a is composed of many different size of microrods. According to the scale, the length of sample a is in the range of 2.77-11.69μm, and the diameter is between 0.62μm and 4.92μm. The sample a have a typical single-phase wurtzite structure with c-axis preferred orientation and with smooth surface. From Figure 2c we can see that the microrods mainly have two surface topography. One is the single wurtzite with smooth surface, another one is multilayer microrods. Figure 2b and d clearly demonstrates that sample b consist of different length of microwires. Compare to the scale the length of the microwires is in the range of 7.33-57.33μm. The diameter of the microwires have small difference, one is about 0.5μm and another one is about 1.0μm, it is more likely that during the growth process, two single microwires were growing together. From the SEM image the structure of the microwires were more different than the microrods, the side wall of the microwires were smoother without any edges and corners. The microwires have no regular arrangement.
Figure 2. The SEM image of ZnO microrods and microwires.

The structure properties of the two samples were tested by XRD which is shown in Figure 3, the samples were mixed up together to do the test. It can be seen from the figure, there are four peaks that named ZnO (002), (102), (110) and (103) peaks which located at 34.36°, 47.55°, 56.67°, and 62.69° separately. The (002) peak can give some information about structure properties, the intense (002) peak means that the samples were grown up along the c-axis which agree with the SEM results. The lattice constant can be calculated as follows:

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

(1)

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

(2)

The incident light wavelength \(\lambda=0.15418\text{nm}\), \((hkl)\) represent Miller index, \(\theta\) is the diffraction angle, according to the formula 1 and (002) peak, the lattice constant \(c=0.5219\text{nm}\). At the same time, combined formula 2 with (110) peak, the lattice constant \(a=0.3248\text{nm}\). In theory, the lattice constant of hexagonal wurtzite structure ZnO are \(a=0.3427\text{nm}\), \(c=0.5200\text{nm}\). The experimental results are very close to the theoretical results which means the samples were present hexagonal wurtzite structure and grown up along the c-axis.
Figure 3. The XRD pattern of the samples.

The growth mechanism of the two samples can be described as follows. First of all, the schematic diagram of the ZnO microrods was shown in Figure 4. During the whole progress, the ZnO powder, carbon powder and oxygen would occur redox reactions which can be expressed as:

\[
\begin{align*}
ZnO + C &= Zn + CO \quad (3) \\
2CO + O_2 &= 2CO_2 \quad (4) \\
2Zn + O_2 &= 2ZnO \quad (5)
\end{align*}
\]

Before oxygen supply, the ZnO powder was reduced to zinc. When growth temperature up to 800°C, the oxygen is inlet, zinc atom reacts with oxygen atom to generate ZnO seed, just as Figure 4 A. As time goes by, the microrods was growth along the seed layer which getting longer and wider. Then there are two different structures comes up. One is common nanostructures which is present in Figure 4C, the microrods have smooth surface with wurtzite structure, the microrods growth along the c-axis without any defect. Another one is composite multilayer nanostructures. At first stage, the ZnO seed layer was formed, the second layer of the microrods was grown up around the seed layer’s outside surface, just as the Figure 4D shows. It’s also possible to grow for a third layer or a fourth layer. It is turned out that the speed of crystal growth of the microrods is different, then the microrods formed to be pencil-cone micro-rods. The growth mechanism of ZnO microwires also be shown in Figure 5. There are two different structures emerged in the figure, one is the normally microwires, the seed layer formed to be single wires with smooth outside surface which is shown in Figure 5 ABC, another one is the double microwires structures, the mechanism maybe that, at the beginning, the two microwire seed layers were grown up together which makes them to be one seed layer, then the microwires become more longer and longer with clean and smooth surface. The microrods and microwires were grown up under the same condition, but the morphology was different, the possible causes can be described as: on the one hand, the two samples are collected at different place, the substrate temperatures are not the same. The sample a is close to the heating zone, and the sample b is in the air which is far away from the heating zone, so the growth temperature is different between the two samples. Another reason maybe that, the mix gas of oxygen and nitrogen is go through the quartz tube, the concentrations are different, there are more gas molecules in the upper space, so the growth rate is faster than the lower
one. Once the seed layer was formed, the upper one is more likely to grow up in length and the lower one is likely to grow up in width. These are two reasons for the different nanostructures.

**Figure 4.** The growth mechanism of ZnO microrods. **Figure 5.** The growth mechanism of ZnO microwires

4. Conclusion
To sum up, the ZnO micro-rods and micro-wires were synthesis by simple CVD method. There are two samples collected on the edge of the quartz tube, the upper one was found to be ZnO micro-wires which have two kinds of nanostructures, one is the normally micro-wires with smooth outside surface, another one is double-like ZnO micro-wires. The main reason of the difference is that at the first stage, the two ZnO single seed were close to each other and grow up together. The micro-rods were between 7.33-57.33μm in length and 0.5μm in diameter for single micro-wire and 1.0μm for double-like micro-wire. The lower one is ZnO micro-rods. There are also two kinds of nanostructures in micro-rods, one is the single micro-rods which have typical wurtzite structure, the micro-rods were about 2.77-11.69μm in length and 0.62-4.92μm in diameter. Another one is the composite multilayer nanostructures which much like the pencil--cone micro-rods. The micro-rods were grown up one-layer surrounds another. The two kinds micro-rods all have perfect wurtzite structure without any defects. According to the XRD pattern, the lattice constants are calculated to be a=0.3248nm and c=0.5219nm which means the samples are have hexagonal wurtzite structure. The growth mechanism of the two samples also discuss in detail. The possible reasons for the two morphology structures are the substrate temperature and the concentration of the mixed gas.

Acknowledgments
This work was financially supported by the Science Public Welfare Research Fund of Liaoning Province (No.2020JH4/10100039); Science and Technology Funds from Liaoning Education Department (No. QL201904); Nature Science Foundation of Liaoning Province (No. 20180540079).

References
[1] Zou A L, Qiu Y, Yu J J, Yin B, Cao G Y, Zhang H Q and Hu L Z 2016 Sensor Actuat. B 227 65-8
[2] 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
[3] Liang S, Sheng H, Liu Y, Huo Z, Lu Yand Shen H 2001 J. Cryst. Growth 225 110-3
[4] Tsukazaki A et al 2004 Nat. Mater. 4 42-6
[5] Tsukazaki A, Kubota M, Ohtomo A, Onuma T, Ohtani K, Ohno H, Chichibu SF and Kawasaki M 2005 Japan J. Appl. Phys., Part 2 44 643-5
[6] Yin B, Qiu Y, Zhang H, Ji J and Hu L 2014 *Cryst. Eng. Comm.* **16** 6831
[7] Yin B, Qiu Y, Zhang H, Ji J and Lei J 2015 *J. Mater. Sci. Mater. Electron.* **26** 742-6
[8] Chen Y, Xu P C, Xu T, Zheng D and Li X X 2017 *Sensor. Actuat. B* **240** 264-72
[9] Eixenberger J E et al 2019 *ACS Appl. Mater. Interface.* **11** 24933-44
[10] Xie A, Yang D D, Li Y M and Zeng H B 2019 *J. Mater. Chem. C* **7** 29
[11] Lou Z, Chen S, Wang LL, Jiang K and Shen G Z 2016 *Nano Energy* **23** 7-14
[12] Ma Y, Liu N, Li L, Hu X, Zou Z, Wang J, Luo S and Gao YA 2017 *Nat. Commun.* **8** 1207
[13] Tian H, Shu Y, Wang X F, Mohammad M A, Bie Z, Xie Q Y, Li C, Mi W T, Yang Y and Ren T L 2015 *Sci. Rep.* **5** 8603
[14] Jia J, Huang G, Deng J and Pan K 2019 *Nanoscale* **11** 4258–66
[15] Kweon O Y, Lee S J and Oh J H 2018 *NPG Asia Mater.* **10** 540–51
[16] An B W, Heo S, Ji S, Bien F and Park J U 2018 *Nat. Commun.* **9** 2458
[17] Wang L L, Jackman J A, Tan E L, Park J H, Potroz M G, Hwang E T and Cho N J 2017 *Nano Energy* **36** 38–45
[18] Cheng A J, Tzeng Y H, Zhou Y, Park M and Lee W 2008 *Appl. Phys. Lett.* **92** 092113
[19] Kim S W and Fujita S 2005 *Appl. Phys. Lett.* **86** 153119
[20] Fan Z Y, Dutta D, Chien C J, Chen H Y and Brown E C 2006 *Appl. Phys. Lett.* **89** 213110
[21] Zou C W, Liang F and Xue S W 2015 *Appl. Surf. Sci.* **353** 1061-9
[22] Behera B and Chandra S 2016 *Sensor Actuat. B.* **229** 414-24
[23] Greene L E, Yuhas B D, Law M, Zitoun D and Yang P D 2006 *Inorg. Chem.* **45** 7535-43