

Systematic Study on Experimental Conditions for Large-Scale Growth of Aligned ZnO Nanowires on Nitrides

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In vapor–liquid–solid (VLS) growth, it is generally believed that nanowires would grow as long as the right catalysts and substrate are supplied as well as the growth temperature is adequate. We show here, however, that oxygen partial pressure plays a key role in determining the quality of the aligned ZnO nanowires. We present a “phase diagram” between the oxygen partial pressure and the growth chamber pressure for synthesizing high quality aligned ZnO nanowires on GaN substrate. This result provides a road map for large-scale, controlled synthesis of ZnO nanowires on nitride semiconductor substrates with the potential to meet the needs of practical applications. The chemical process involved in the growth process is also systematically elaborated based on experimental data received under different conditions.

Recently, quasi-one-dimensional (1D) ZnO nanostructures such as nanobelts,¹ nanowires,² nanorods³ and nanosprings/nanorings⁴ have attracted a lot of research interest due to their shape induced unique electrical and optical properties for applications in sensors,⁵ optoelectronics,⁶ field emissions,⁷ and logical circuit devices.⁸ Growth of ZnO nanostructures has been one of the most active fields in nanotechnology.⁹ Fabrication of vertically aligned ZnO 1D structures is considered to be an effective approach for nanodevices assembly and applications on light emitting¹⁰ and field emission.¹¹ Aligned growth of ZnO nanowires can be achieved by various methods, such as vapor–liquid–solid (VLS) process,¹² metal–organic chemical vapor deposition (MOCVD)¹³ or sol–gel process.¹⁴ As the simplest and most efficient method, VLS process has been employed by many researchers for growing aligned ZnO nanorods on various substrates, such as silicon,¹⁵ sapphire,^{10,16} GaN,^{17,18} and AlGaN/AlN.¹⁹ However, the growth conditions reported are quite diverse and without a consistent pattern. For instance, some were grown under high vacuum,^{2,10} whereas some were grown close to one atmosphere;²⁰ some substrates were put on the source materials,¹⁷ whereas some substrates were put far away from the source.^{10,15,16} As a result, the size of the nanorods and the quality of the alignment varies drastically. There is a lack of a systematic investigation on the experimental conditions under which ZnO nanorods are synthesized reproducibly at a large area.

By VLS, it may be assumed that nanowires would grow as long as the catalysts are supplied as well as the temperature is adequate. In this paper, we show a surprising result that the partial pressure of oxygen plays a key role in determining the quality of the grown ZnO nanowires. By defining different

growth results as different “phases”, we present a “phase diagram” between the oxygen partial pressure and the growth chamber pressure for synthesizing high quality aligned ZnO nanorods on the GaN substrate using VLS process. This result provides a foundation for large-scale, controlled synthesis of ZnO nanorods on nitride semiconductor substrates to meet the needs of practical applications.

In our experiments, an undoped *c*-plane oriented GaN film with a thickness of 2 μm that was grown on an *a*-plane sapphire single-crystal substrate was used as the substrate. A thin layer of gold (7–8 nm) was deposited on the top of GaN via plasma sputtering, which acted as catalysts to guide the growth of ZnO nanorods. The source materials were a mixture of equal amounts (by weight) of ZnO power and graphite power, which was grounded and placed in an alumina boat. Then the boat was loaded in the center of an alumina tube (150 cm long, 4 cm inner diameter), where the substrate was placed 10 cm away from the source material at the downstream side. The tube was placed in a horizontal tube furnace (model F79345 from Barnstead/Thermolyne Co.) with cooling water running through the outside of the tube at the ends. After pumping the system down to 2×10^{-2} mbar, a premixed gas (Ar and O₂) was introduced into the system with a flow rate of 50 sccm to bring the pressure back to a certain point between 1.5 and 300 mbar according to the designed experiments. The furnace was then heated to 950 °C at a heating rate of 50 °C/min and the temperature was held at the peak temperature during the growth for 30 min. Finally, the system was slowly cooled to room temperature under flowing gas. All of the experimental conditions remained fixed during the growth except two variables: the volume ratio of O₂ to Ar gas (1% to 4%), and the chamber pressure (0.3–100 mbar).

The as-synthesized ZnO nanorods were first examined by scanning electron microscopy (SEM). Figure 1a shows a typical image of ZnO nanorods grown on GaN substrate with a good

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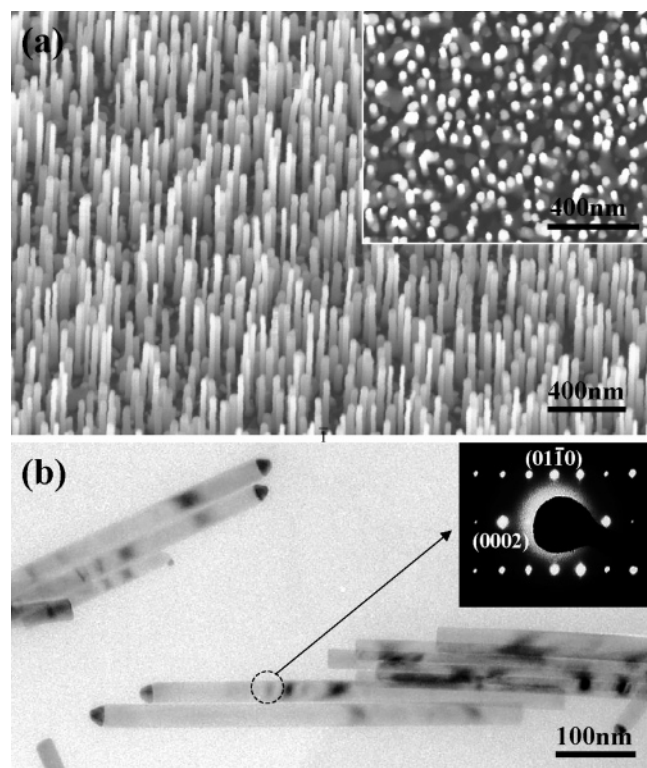


Figure 1. Aligned ZnO nanorods on GaN substrate. (a) Side view SEM image, the inset is the top view SEM image of the sample; (b) TEM image of ZnO nanorods, the inset is an electron diffraction pattern taken from one ZnO rod.

alignment, in which almost all of the ZnO rods have the same lengths and diameters and are oriented perpendicular to the substrate. This sample was grown under the condition of 2% O₂ (by volume) and 30 mbar chamber pressure. The well-aligned structure uniformly covered all of the area of the GaN substrate. The inset in Figure 1a shows a top view of the aligned ZnO nanorods, where only the very bright gold catalyst tips are observed. It also confirms that almost every single nanorod is perpendicular to the substrate and there is no side branch.

The crystallography of ZnO rods is characterized by Hitachi HF2000 transmission electron microscopy (TEM). Figure 1b shows a typical TEM image of the ZnO nanowires/nanorods. Each nanorod is a single crystal and exhibits a uniform thickness. From the ZnO nanorod, a diffraction pattern was recorded as shown in the inset of Figure 1b, which reveals the growth direction is along [0001] and the six sides facets are {11 $\bar{2}$ 0}.

In the experiments, we found the oxygen partial pressure and the system total pressure played key roles in the growth of ZnO nanorods. With different oxygen volume percentage and different chamber pressure, the quality and growth behavior of the ZnO nanowires are strongly affected. We have carried out over 100 growth experiments under different growth conditions, which were designed to quantitatively define the best combination of the O₂ partial pressure and the chamber pressure for growth of aligned ZnO nanowires. For consistency, all of the samples were collected at the 880 °C temperature zone, which is 10 cm away from the source materials.²¹ The O₂ volume percentage in the chamber varied from 1 to 4 vol %, and the system pressure varied from 1.5 to 300 mbar. Since the growth system was first pumped down to 2×10^{-2} mbar, the system pressure was brought back to a growth pressure at a value between 1.5 and 300 mbar, the oxygen coming from the residue air only contributed 0.28–0.0014% toward the entire oxygen content, which was much less than the percentage of O₂ in the

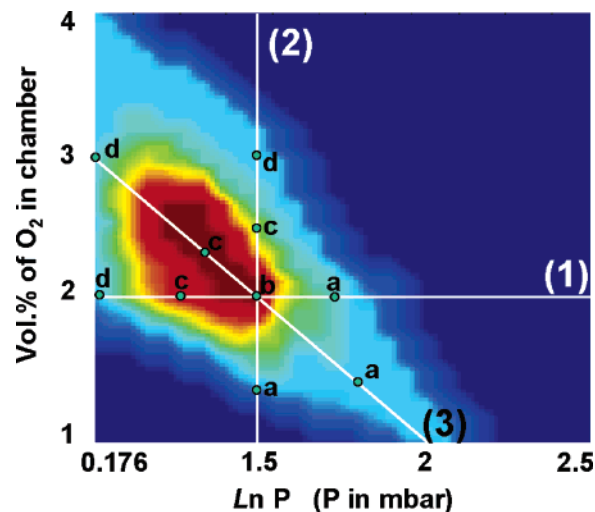


Figure 2. “Phase diagram” that correlates oxygen volume percent in the growth chamber (e.g., partial pressure) and the growth chamber pressure (plotted in logarithm and P is in unit of mbar) for growing aligned ZnO nanorods (see text). This phase diagram was generated from the results of over 100 designed experiments of different conditions. The point matrix was broadened and smoothed by MatLab to form a quasi-continuous phase diagram. The synthesis line (1) is the line with constant oxygen volume percentage; line (2) is the line with constant system pressure; line (3) is the line with linearly varying oxygen volume percentage and system pressure.

flow gas. Therefore, the partial pressure of O₂ was considered to be the volume percentage of the O₂ introduced in the flow gas.

The experimental results are summarized in Figure 2, which is a “phase diagram” for the O₂ volume percentage in the chamber and system pressure, under which the optimum conditions for growing aligned ZnO nanowires are presented. The term of “phase diagram” used here is given a new meaning of representing the “road map” for controlled synthesis of nanowires. This phase diagram was determined for the furnace system described in the Experimental Section. As shown in Figure 2, the horizontal axis is the logarithm of the total chamber pressure; the vertical axis is the oxygen volume percentage in the chamber, and the quality of the grown ZnO nanowires is represented by different colors. The quality of the nanowires is characterized by their uniformity, density, length, and alignment. In the phase diagram, dark red represents the best growth condition, where a perfect alignment of ZnO nanorods with a high density and uniform length and thickness were achieved. The growth is good in the red area, where the density is lower and the nanorods are shorter. In the green and light blue area, the growth is poor, where only a little amount of short nanorods was found. No growth was found in the dark blue region. This phase diagram provides the road map for growing high quality aligned ZnO nanowires.

To clearly demonstrate the effects of total chamber pressure and O₂ volume percentage to the final results, three sequences are highlighted in the phase diagram: fixed O₂ volume percentage but with variable chamber pressure (line 1); fixed system pressure but with variable O₂ volume percentage (line 2); and linear increased O₂ volume percentage with decreasing system pressure (line 3). Four representative points on each line are picked up to present the quality of the grown nanowires under the defined growth conditions.

Figure 3 presents SEM images of four samples received under the conditions of 2% fixed O₂ volume percentage (1 sccm oxygen, 49 sccm argon) but 4 different chamber pressures: 50

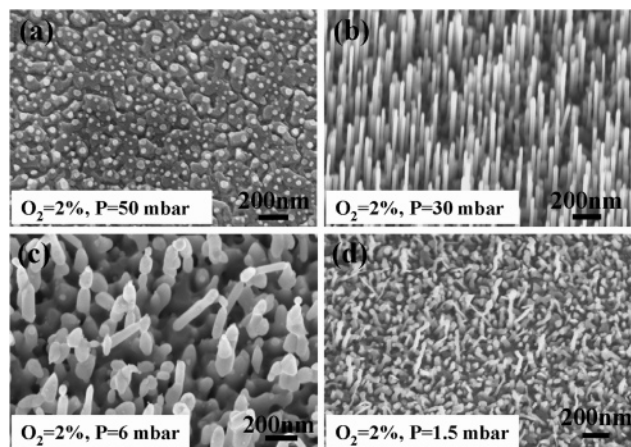
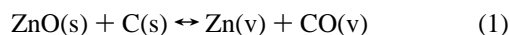


Figure 3. SEM images of ZnO nanorods grown under the conditions of 4 green points along line (1) in Figure 2 under constant oxygen volume percentage (2%) but variable chamber pressure: (a) 50 mbar; (b) 30 mbar; (c) 6 mbar; (d) 1.5 mbar.

mbar, 30 mbar, 6 mbar, and 1.5 mbar as shown in Figure 3a–d, respectively. In Figure 3a, which represents the results with the highest system pressure among the four experiments, no nanowire was formed but only gold catalyst particles were found, which was confirmed by EDS. With the decreasing of system pressure to 30 mbar, a perfect alignment of ZnO nanowires was achieved, as shown in Figure 3b. When the system pressure dropped to 10 mbar, ZnO nanorods became shorter and randomly orientated, as shown in Figure 3c. By further dropping the system pressure to 1.5 mbar, only a few thin nanorods were deposited on a continuous ZnO film. This regular change in the ZnO morphology is contributed to the relative increased Zn vapor concentration while the system pressure decreased.

In the carbon-thermal evaporation process, the Zn vapor source is dominated by reaction



This reaction is favorable in high temperature. Once the vapors are transported to the cooler region where the substrate is located, the Zn vapor is deposited on the surface of the catalyst and reoxidized, resulting in the growth of the nanowire. Since the amount of Zn vapor is determined by the local temperature, thus, the rate at which the Zn vapor is produced can be assumed to be a constant under different chamber pressures. Consequently, when the total system pressure drops, the partial pressure of the Zn vapor increases. When the system pressure is too high, Zn vapor may not reach supersaturation, and thus, no deposition occurs on the surface of the catalyst particles, resulting in no growth at all (Figure 1a). When the system pressure is too low, Zn vapor may be over supersaturated, the vapor deposits not only on the surface of the Au catalyst but also the surface of the GaN substrate, resulting in formation of nanowires as well as a thin film on the substrate surface (Figure 4d). High quality aligned ZnO nanorods can only be achieved when a reasonable supersaturation level of Zn vapor is reached at a moderate system pressure, which is around 30 mbar under our growth condition.

The effect of O_2 partial pressure is illustrated in Figure 4, in which SEM images of a–d represent the typical results of ZnO deposition at O_2 volume percentage of 1.3%, 2%, 2.5%, and 3%, respectively, with a fixed chamber pressure of 30 mbar. At a very low O_2 volume percentage (1.3%), only small ZnO dots were nucleated, as shown in Figure 4a. By increasing the

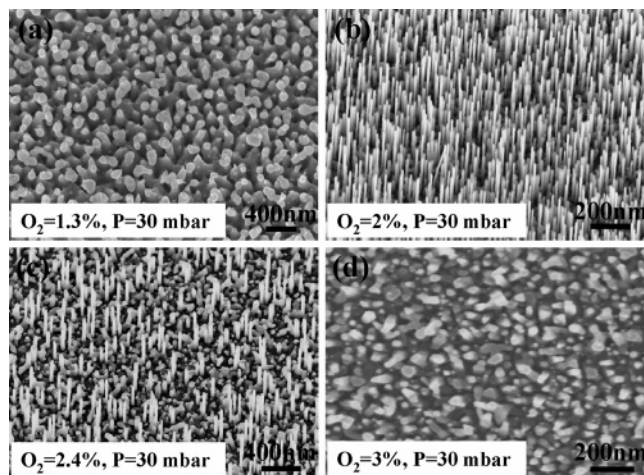
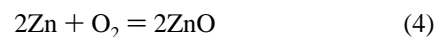
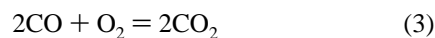


Figure 4. SEM images of ZnO nanorods grown under the conditions of 4 green points along line (2) in Figure 2 under constant chamber pressure (30 mbar) but variable oxygen volume percentage: (a) 1.3%; (b) 2%; (c) 2.4%; (d) 3%.

O_2 volume percentage to 2%, good alignment of ZnO nanowires was achieved (Figure 4b). When the O_2 volume percentage increased to 2.5%, as shown in Figure 3c, the density of ZnO nanorods dropped dramatically, as well as their lengths. The growth of ZnO nanorods almost vanished once the O_2 volume percentage was set at 3% (Figure 4d).

There are three possible reactions that O_2 is involved in carbon assisted thermal evaporation process



Zn vapor is still provided by eq 1. From the Ellingham diagram, reaction 1 occurs only when the temperature is higher than 970 °C, whereas in our experiments, the furnace was just heated to 950 °C; thus, the question is what makes the local temperature high enough for reaction 1 to be possible? In the beginning when there was no other gas in the system, the main reaction involving O_2 is reaction 2, which generated heat as well as CO. The heat could be absorbed locally by the source materials (ZnO plus graphite) and possibly facilitate reaction 1 to produce Zn vapor. On the other hand, local concentration of CO could also increase, which could hinder the Zn vapor generation. Under the influence of these two effects, reaction 1 cannot be fully accelerated, and as a result, when the O_2 partial pressure was very low, insufficient Zn vapor was released to reach a reasonable supersaturation point for producing ZnO nanorods, as the situation shown in Figure 4a.

Once the partial pressure of O_2 was increased, additional O_2 can react with CO to form CO_2 (eq 3), which lowered the concentration of CO and generated heat as well. Both of these two effects facilitated reaction 1. Therefore, supersaturation of Zn vapor can be reached, leading to growth of high quality aligned ZnO nanorods, as shown in Figure 4b. However, when the partial pressure of O_2 was further increased, additional O_2 could react with Zn vapor generated from the source materials immediately to form a ZnO film/grain. We have examined this situation by introducing a lot more O_2 into the system and found a layer of large ZnO nanorods/grain was formed on the surface of the source powders. Consequently, the Zn vapor decreased again near the substrate and little growth was found (Figure

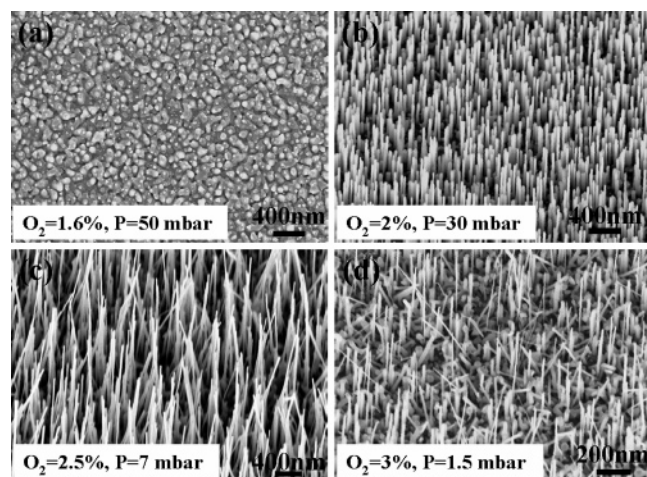


Figure 5. SEM images of ZnO nanorods grown under the conditions of 4 green points along line (3) in Figure 2 by linearly adjusting the chamber pressure and oxygen partial pressure. (a) 1.6% oxygen volume percentage, 50 mbar chamber pressure; (b) 2% oxygen volume percentage, 30 mbar chamber pressure; (c) 2.5% oxygen volume percentage, 7 mbar chamber pressure; (d) 3% oxygen volume percentage, 1.5 mbar chamber pressure.

4d). In general, only moderate O₂ volume percentage (~2 vol %) results in good aligned ZnO nanorods.

Four typical results of ZnO deposition carried out under linearly increased O₂ partial pressure with decreased chamber pressure are illustrated in Figure 5. The experimental conditions selected are as follows: (a) 1.6% O₂ at 50 mbar system pressure; (b) 2% O₂ at 30 mbar system pressure; (c) 2.5% O₂ at 7 mbar system pressure; (d) 3% O₂ at 1.5 mbar system pressure. Except point a, where both O₂ partial pressure and system pressure were intended to give a low Zn vapor concentration, all of the other three points in the phase diagram exhibited a reasonable growth of ZnO nanorods. This is because the decreasing of Zn vapor caused by increased O₂ could be compensated by reducing the chamber pressure; thus, the reasonable supersaturation level of Zn vapor can be maintained in a relatively large range.

In summary, we reported a “phase diagram” that correlates the partial pressure of oxygen with chamber pressure for growing aligned ZnO nanorods on GaN substrate via VLS process. Distinct from the conventional understanding about VLS growth process, we found that both the partial pressure of O₂ and total system pressure exhibited distinct effects on the final morphologies of deposited ZnO nanostructures. In our

furnace system, the optimal condition for growing aligned ZnO nanorods was found to be 2% O₂ at 30 mbar system pressure at a local growth temperature of 880 °C. The phase diagram presented here can provide a road map for growing aligned ZnO nanowires at a large-scale.

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- (21) It is possible to observe deposition on other temperature zone while the experimental conditions are changed. However, our study was carried out under specifically defined conditions in order to determine the “phase diagram”.