Effects of Flow Transport of the Ar Carrier on the Synthesis of ZnO Nanowires by Chemical Vapor Deposition

Joon Hyock Choi¹², Ju Seok Seo³, Seung Nam Cha¹, Hyun Jin Kim¹, Seong Min Kim¹⁺, Young Jun Park¹, Sang-Woo Kim³, Ji-Beom Yoo²⁷, and Jong Min Kim¹

¹Frontier Research Laboratory, Samsung Advanced Institute of Technology, Yongin, Gyeonggi 446-712, Republic of Korea
²SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 440-746, Republic of Korea
³School of Advanced Materials Science and Engineering, SKKU Advanced Institute of Nanotechnology (SAINT), Center for Human Interface Nanotechnology (HINT), Sungkyunkwan University, Suwon 440-746, Republic of Korea

Received August 10, 2010; revised October 5, 2010; accepted October 6, 2010; published online January 20, 2011

ZnO nanowires were synthesized by the chemical vapor deposition (CVD) and heating of ZnO powders under Ar gas flow. The effect of the carrier gas (Ar) on the growth region inside the CVD chamber was systematically investigated. The transport of Zn vapor was assisted by the Ar gas flow, producing a spatial distribution of the growth of the ZnO nanowires (in this case, the longer nanowires grown in a certain region show better crystallinity). A simple model of a parabolic transport of Zn vapor (caused by the Ar flow) was, thus, proposed to explain these effects. Field-effect transistors (FETs) were also fabricated using ZnO nanowires and the device performance was determined, showing a mobility of 20 cm²/V·s⁻¹.

1. Introduction

ZnO nanowires, having a wide band gap (~3.27 eV) at room temperature and a large exciton binding energy (~60 mJ) are interesting semiconductor materials. Because of these remarkable physical and optical properties, the ZnO nanowires have attracted much attention and become a strong candidate for application in many devices such as photovoltaic cells, sensors, nanolasers, and ultraviolet (UV) light emitting diodes. Several growth techniques were used to grow the ZnO nanowires—namely, the hydrothermal method, chemical vapor deposition (CVD), and laser-assisted vapor phase synthesis. In spite of much interest in these ZnO nanowires, less attention has been paid to the effect of the carrier gas on the CVD growth of nanowires using a furnace.

In this study, ZnO nanowires were synthesized by heating ZnO powders (~950 °C) under different Ar gas flow rates (30–50 sccm). The effect of the carrier gas on the growth region of the nanowires was systematically investigated. A simple model of parabolic transport of Zn vapor was proposed to explain the growth region of the ZnO nanowires. In this model, the vertical velocity of Zn vapor is simulated to be almost the same as the horizontal input velocity of Ar gas (as a constraint) to explain our experimental observation. The transported Zn vapor then forms a spatially distributed growth of the ZnO nanowires along the length and crystallinity of the ZnO nanowires was determined using the PL spectrum. The longest ZnO nanowires show the largest crystallinity of the nanowires.

2. Experimental Procedure

ZnO nanowires were thermally grown using a horizontal quartz tube (diameter: 2.1 cm) by vaporizing ZnO+C (1:1) powder. A c-plane sapphire substrate was used on which a 3-μm-thick Au thin-film catalyst was deposited using a thermal evaporator. The source powder and series of Au coated substrates (1 × 1 cm²) were then placed on a ceramic boat. The substrates were located 2–8 cm away from the powder in this case. Then the ceramic boat was loaded at the center of the tube. The ZnO nanowires were synthesized at a temperature of ~950 °C for 40 min under different Ar gas flow rates (30, 40, and 50 sccm). The total gas pressure inside the quartz tube is equal to atmospheric pressure. The morphology of the as-grown nanowires was characterized using field emission scanning electron microscopy (FESEM; Hitachi S-4500). The photoluminescence (PL) spectrum was also measured using a He–Cd laser with an excitation wavelength of 325 nm. A ZnO nanowire FET was fabricated by transferring the nanowires onto a silicon wafer with a 200 nm thick thermally grown oxide (as a back gate) using a contact printing method. The source and drain electrodes were defined by photolithography and a 250 nm thick Nb metal electrode was deposited by sputtering. The distance between the source and the drain was ~3 μm. The electrical properties of ZnO nanowire FETs were measured using a semiconductor parameter analyzer (Keithley PS-6-150).

3. Results and Discussion

Figures 1(a)–1(c) show SEM images of the ZnO nanowires grown at ~950 °C under a 50 sccm Ar flow rate. The substrates were positioned at 5, 7, and 8 cm from the mixture of the ZnO and C powders. This shows that the length of the nanowires changed with the position (5–8 cm). The maximum length of the nanowires (~14 μm) was obtained at a point 7 cm from the source and the length of the nanowires decreased as moved away from the (optimum) position (~7 cm from the source here): the nanowire length observed were ~8 μm at 5 cm and ~11 μm at 8 cm. The crystallinity of the nanowires was investigated using the PL spectrum. The longest ZnO nanowires show the largest intensity ratio of the UV emission peak to the green emission peak, i.e., the highest crystallinity, as shown in Fig. 2(a). The distribution of the crystallinity (i.e., the intensity ratio of the UV emission to green emission peak) is also observed at lower flow rate (e.g., 40 sccm) as shown in Fig. 2(b). Figures 1(d)–1(f) show SEM images of the ZnO nanowires grown at different positions (2, 4, and 7 cm respectively) at different Ar flow rates (30, 40, and 50 sccm respectively). Clearly, it shows that the growth position is correlated/proportional to the flow rate of the Ar gas such that the growth region of the nanowires moves farther from the source with increasing flow rate.
A simple model of the parabolic transport of Zn vapor is first suggested to quantitatively explain this phenomenon, although gas flow dynamics with a temperature gradient in CVD have been reported.\textsuperscript{12–14} During the evaporation, ZnO powder can be thermally decomposed into Zn and O atoms though \(2\text{ZnO} \rightarrow 2\text{Zn} + \text{O}_2\).\textsuperscript{15} This solid-phase Zn is then vaporized at 907°C (i.e., melting temperature) under the atmospheric pressure (~10\(^5\) Pa). Ideally, the vaporization velocity of molecules can be estimated using the Hertz–Knudsen Langmuir equation.\textsuperscript{16} In this equation, Zn and O\(_2\) are assumed to be ideal gases, indicating the lack of interaction between individual molecules. However, in our growth process, the actual velocity of Zn vapor (\(v_y\)) could be much lower than the vaporization velocity (\(v_{\text{vapor}}\)) such that \(0 < v_y < v_{\text{vapor}}\), where \(v_{\text{vapor}} \approx 72.6\, \text{m/s}\).

In the CVD process, the Ar flow is essential for Zn vapor to be transported into the growth region where the substrates are placed. A classical parabolic model is used to describe this and the following equations are used.

\[
x = v_y \times t \tag{1}
\]
\[
y = v_y \times t - a \times \frac{t^2}{2} \tag{2}
\]

where \(x\) (horizontal) and \(y\) (vertical) give the trajectory of the particles, \(v_y\) is the vertical velocity, \(v_x\) is the horizontal velocity, and \(a\) is the acceleration of the Zn vapor particles. Here, two variables (i.e., vertical velocity and acceleration of the Zn vapor) are numerically adjusted to fit the experimental growth region obtained (i.e., 2–4 cm for 30 sccm, 3–5 cm for 40 sccm, and 5–8 cm for 50 sccm). Firstly, the vertical velocity of Zn, \(v_y\), is assumed to be within the range.

![Fig. 1.](image1)

![Fig. 2.](image2)
of the horizontal velocity of the Ar flow \((v_{Ar})\) such as 

\[ v_{Ar} - \delta_1 < v_y < v_{Ar} + \delta_2 \]

with some variations \(\delta_1\) and \(\delta_2\). Secondly, the horizontal velocity of Zn is mainly subjected to the velocity of the Ar flow. The velocity of the Ar flow can be calculated using formulas such as

\[ v_{Ar} = 4Q/(\pi d^2) \]

where \(Q\) is the actual flow rate expressed under actual temperature and pressure [i.e., \(Q = Q_0 T_0 P_0/(T\_0 P)\) where \(Q_0\), \(P_0\), and \(T_0\) are the flow rate, pressure, and the temperature under the standard conditions] and \(d\) is the diameter of the tube. The calculated velocities of the Ar flow are then \(~0.0014\) m s\(^{-1}\) for 30 sccm, \(~0.0019\) m s\(^{-1}\) for 40 sccm, and \(~0.0024\) m s\(^{-1}\) for 50 sccm at a furnace temperature of 950 °C under atmospheric pressure (~1 atm).

Thirdly, the vertical acceleration, \(a\) is numerically calculated/fitted to be \(~1.6 \times 10^{-4}\) m s\(^{-2}\).

For example, in the case of 50 sccm Ar (i.e., \(v_x \sim v_{Ar} \sim 0.0024\) m/s), with the vertical velocity of the Zn \((v_y \sim 0.0024\) m/s\(^{-1}\)), the simulated parabolic curve explains the growth point of ~7 cm. With a certain variation from this velocity [i.e., from \(v_y \sim 0.0006\) (\(\approx \delta_1\)) to \(v_y \sim 0.0003\) (\(\approx \delta_2\)) m s\(^{-1}\)], the broad growth region can be described as shown in Figs. 1(a)–1(c) and 3(a). This result is well matched with the experimentally obtained growth region. This variation is less than 25% for the three gas flow rates. The simulated parabolas with respect to different Ar flow rates of 30, 40, and 50 sccm are shown in Fig. 3(b). The intersection between the parabolas and the x-axis is well matched with the growth region where the longest ZnO nanowires were obtained, as shown in Figs. 1(d)–1(f). This shows that the higher flow rate of the carrier gas can shift the growth point further away from the source region and vice versa. Note that the numerically obtained low acceleration could be explained by the effect of an upward thermal drift (in the opposite direction to gravity) during the high-temperature growth (~950 °C).

Figures 4(a) and 4(b) show the output and transfer curve of the ZnO nanowire FETs with the back-gate configuration. The ZnO nanowire FET has a 3 μm channel length, a 200 nm thick gate insulator (SiO\(_2\)), and a 100 nm channel width. The diameter of the nanowire is 100 nm. Ten nanowires were transferred from the optimum region. The electrical performance was measured using a four-probe measurement system (Keithley 4200) in an ambient environment (at room temperature in the dark). Figure 4(a) shows the drain current vs gate voltage \((I_{ds}-V_{gs})\) transfer characteristic at \(V_{ds}\) of 10 V. Figure 4(b) shows the drain current vs drain voltage \((I_{ds}-V_{ds})\) output characteristics as a function of gate voltage.
The gate transfer characteristic shows an on/off ratio of $\sim 10^6$ with an off current of $\sim 10^{-10}$ A, a subthreshold slope of 1 V/decade, and a threshold voltage ($V_{th}$) of $-6$ V. The transconductance ($g_{m}$) is 13.8 $\mu$S and mobility is 20–220 cm$^2$ V$^{-1}$ s$^{-1}$. Note that four point probe measurements at different growth points (for example, 5, 7, and 8 cm at 950 °C/50 sccm) in the dark give a resistivities of 0.64, 0.45, and 0.59 $\Omega$ cm respectively, indicating that the ZnO nanowires grown at optimum position of $\sim 7$ cm has a relatively low resistivity.

4. Conclusions

In conclusion, ZnO nanowires were synthesized by thermal chemical vapor deposition. The effect of the Ar as a carrier gas inside the CVD chamber has been systematically investigated. The results showed that the ZnO growth region moves farther from the source as the gas flow rate increases (up to $\sim 50$ sccm). The optimum length and the crystallinity of ZnO nanowires were observed within the growth region. A model of the parabolic transport of Zn vapor was used to simulate and understand these phenomena.

6) Q. Zhang, Y. Wang, H. Sun, and J. Wu: Conf. Lasers and Electro-optics (CLEO), 2006, CThB