

Synthesis of Uniform ZnO Nanowire Arrays over a Large Area

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ABSTRACT

It has been found that Zinc oxide (ZnO) nanowires have great potential in many applications. Currently, the most commonly used method to grow ZnO nanowire is the vapor transport method. The morphology of the ZnO nanowire is related to the substrate temperature gradient and gas flow dynamic. Previously a uniform ZnO nanowire array could be obtained only on a small area less than 0.5 inch by 0.5 inch due to the temperature gradient between the source and substrate temperatures. This paper reports a novel growth system design that utilized a separated heater to heat up ZnO solid source and uses a three zone furnace to get a uniform temperature across a large area substrate (2 inches by 2 inches). The reacting gas (O₂) can be introduced into system in different ways allowing more efficient utilization of the source material. Here we demonstrated the growth of uniform ZnO nanowire array on Si and sapphire substrate and ZnO nanowire on graphite flake over large area. The ZnO source material and substrate can be well controlled in a wide range of temperatures in order to obtain the optimum growth conditions. The reacting gas (O₂) can be introduced into system at different locations to improve growth efficiency.

Keywords: ZnO, nanowire, large area, vapor transport method

INTRODUCTION

ZnO nanowire is a one-dimensional, single crystalline and self-organized SEMiconductor [1] [2]. Based on its great properties, ZnO nanowire has been reported as a potential material for many applications, such as nanoscaled electronic, chemical, and photonic devices [3]-[8]. Especially, its wide band gap (3.37 eV) and the large exciton binding energy [9] [10], make ZnO nanowire a promising material for optoelectronic applications [3] [9]-[11]. Currently, vapor transport is the most common method used to grow ZnO nanowire [12] [13]. In this method, ZnO vapor is generated by heating up source material (ZnO powder) at higher temperature zone and transported to lower temperature zone where it reacted with reacting gas and condensed on the substrate [3] [11]-[16].

Banerjee and his coworker's research shows that the morphology of ZnO nanowire primarily related to the process pressure, substrate temperature gradient and gas flow [17] [18]. Previously, the substrate is placed on a furnace zone where temperature drops dramatically, uniform ZnO nanowire array could only be obtained over a small area less than 0.5 inch by 0.5 inch [16] [17]. Obviously, such a small uniformity area can not meet the requirement for scaling up of ZnO nanowire devices to higher volume production

In this paper, we have demonstrated the growth of uniform ZnO nanowire arrays on Si and sapphire substrates and ZnO nanowires on graphite flakes over a large area. Photoluminescence measurement over 49 points on the 2 inch sapphire substrate also proves the uniformity of ZnO nanowire.

In addition, this method can also be applied to GaN, In₂O₃ and many other nanowire materials as well. It provides an inexpensive and robust process for making nanowire based devices over large area.

EXPERIMENTAL SETUP

ZnO nanowire was synthesized by a vapor transport method on an EasyTube® 2000ss CVD system (First Nano). The experimental setup is constructed by a solid source heater, a three-zone furnace, gas injector, vacuum pump, and quartz tube. ZnO powder (Alfa Aesar, 99.99%) and graphite powders (Alfa Aesar, 99%) were well mixed as the source material with an atomic ratio of 1:4 and placed at the higher temperature region inside the quartz tube. The source material was placed in a quartz boat placed above the solid source heater which can be heated up to 1100 C. The collecting materials, Si (100) wafer, sapphire wafer or graphite flake (Alfa Aesar, 99.9%) were placed at the lower temperature region about 5 inches away from the source material to collect ZnO nanowire. The carrying gas (Ar) and reacting gas (O₂) were introduced into the quartz tube without or with various lengths (11, 12, and 13 inch) of injectors. All components were placed in the same process tube. Figure 1 shows the schematic of experimental setup. In order to get a uniform temperature across the substrate at the collection area, each zone of the furnace has a respective heater which can be controlled independently to obtain higher and lower temperature regions.

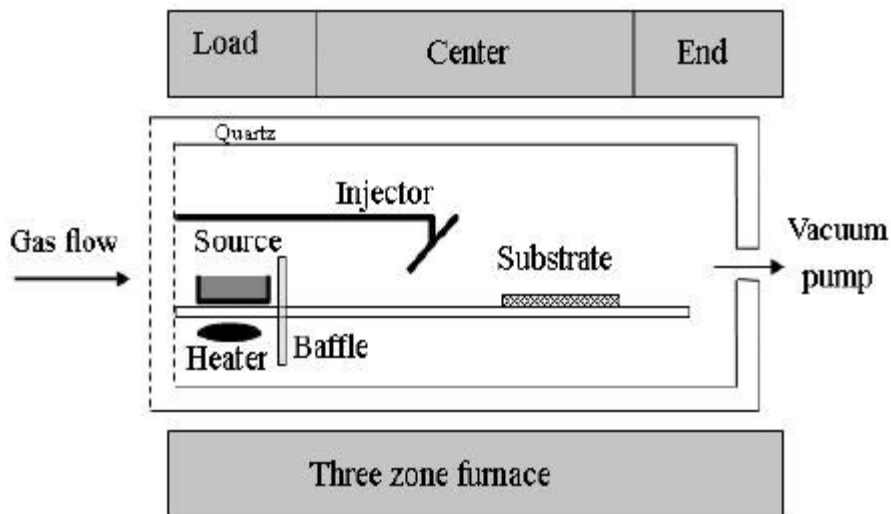


Figure 1: Schematic of experimental setup

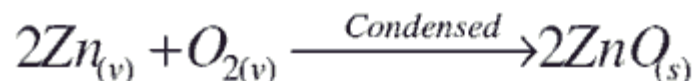
During the growth, the load zone and the solid source heater were set at 975 °C (actual temperature measured by thermocouple under solid source is around 940 °C) to vaporize the source material and the center and end zone temperature were set to control the collection area temperature stable between 700 °C to 830 °C. The substrates, a 2 inch Si (100) wafer, or a 2 inch sapphire wafer, or graphite flake on 3 inches by 2 inches quartz boat, was placed at deposition area (about 5 inches away from the source) where temperature was uniform over a distance of 3 inches. Si wafer and sapphire wafer were coated with Au film (1, 2, and 3 nm) as the catalyst. Carrier gas (Ar) and reacting gas (O₂) were introduced into the quartz tube by a gas injector that was placed at about 2.5, 3.5, and 4.5 inches away from source with Ar to O₂ flow ratio of 10. Within 30 to 60 minute growth time, the whole tube was maintained at a pressure of 2 or 5 Torr. After the growth phase, the entire substrate was covered by ZnO nanowire and

the color turned into gray. The morphology of the as grown samples was studied by scanning electron microscopy (SEM) and Photoluminescence (PL).

DISCUSSIONS

It has been well studied that the morphology of ZnO nanowire is related to the growth temperature. We also obtained these results from our previous experiments, which indicate the temperature uniformity plays an important role in this experiment. Figure 2 shows the system temperature profile was measured by a mobile thermocouple inside the process tube to obtain the actual temperature during growth. By adjusting four individual heaters (solid source, load, center, and end), we successfully controlled the growth temperature uniformity $\pm 5^\circ\text{C}$ at the lower temperature limit (700 to 760°C) and $\pm 1^\circ\text{C}$ at the higher temperature limit (780 to 820°C) over a distance of 3 inches at the collection area.

The source material was vaporized by the below reaction at high temperature, and Zn vapor reacted with O₂ to form ZnO vapor and condensed at lower temperature. These reactions are listed below.



When the process gases are introduced into the system without an injector, O₂ could react with carbon powder or carbon monoxide gas and form CO₂ at the load zone which reduced the amount of O₂ available to react with Zn vapor and decreased the efficiency of vapor transitive. Moreover, some ZnO vapor will condense at center zone while the temperature starts dropping, and this situation caused a deficiency of ZnO condensing on the stern of substrate. By using a gas injector to introduce the process gases into system directly we avoided the reaction between O₂ and carbon powder and CO.

Although the process pressure range is close to medium vacuum, due to the high gas flow speed, a proper diffusion distance is needed for better uniformity of reactant distribution. However, the injector can not be too far away from substrate otherwise the density of ZnO nanowires will be lower on the rare area than the front area. By adjusting the length of the injector, we have improved the uniformity of ZnO nanowire on the substrate and the efficiency of vapor transport.

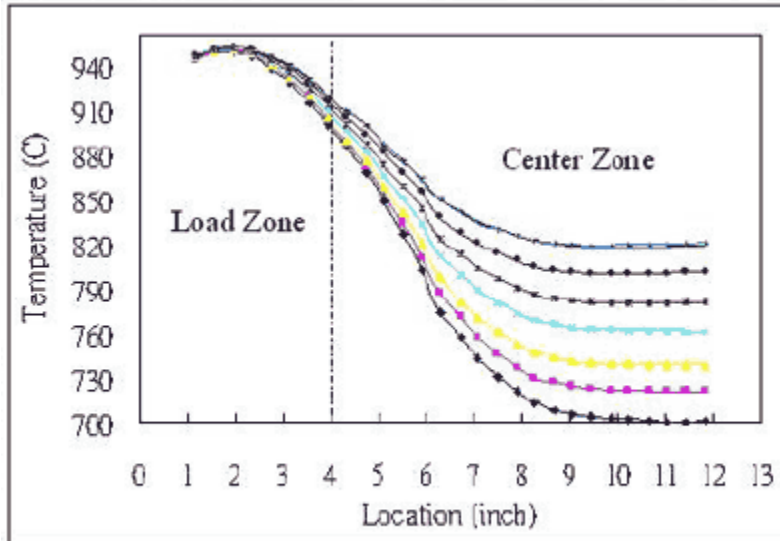


Figure 2: Temperature profile during growth

SEM images have been taken on every 2 mm across the sample, the morphology of ZnO nanowires do not have any sensible change. The cross section SEM images (figure 3 a and b) indicate the ZnO nanowire array grown on the sapphire and Si wafer are vertical aligned to the substrate. The ZnO nanowires dimensions are about 5 μm in length and 50 nm in diameter on all three substrates from 820 $^{\circ}\text{C}$ growth temperature for 45 minutes. However, from the figure 3 c, we can find that using graphite flake substrate to collect material, the density and uniformity of ZnO nanowires is lower than other two samples grown on wafer, and that may come from the non-uniform surface of graphite flake.

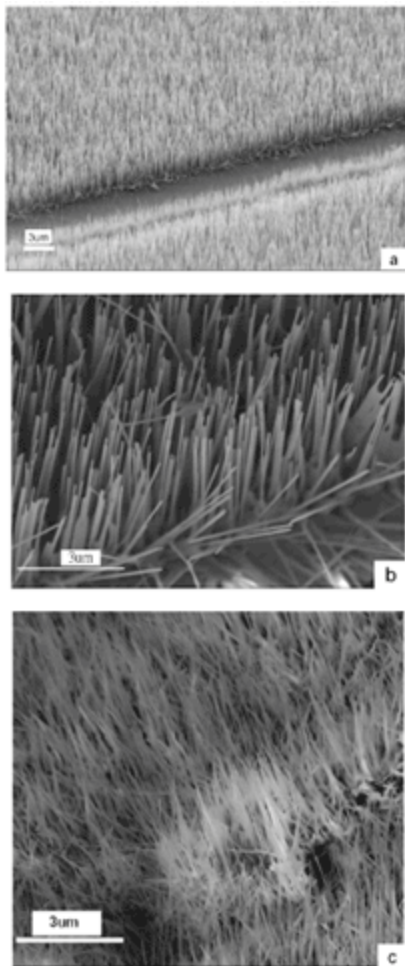


Figure 3: SEM image of ZnO nanowire a) on sapphire wafer, and b) on silicon wafer c) on graphite flake grown at 820°C for 45 minute

PL was measured by Horiba NanoLog system. Samples at room temperature (RT) were excited by 325 nm light source with 1 nm band pass. The excitation power is about 1 μ W with an excitation area of 1 x 5 mm², resulting in a very weak excitation power density of 20 μ W/cm². To shed light on the origin of the broad peak at 515 nm, PL spectra were taken under identical conditions for as-grown samples, O₂ - 400 C – 1 h and H₂ - 400 C – 1 h annealed samples on Si substrates. As displayed in Figure 4, the PL spectrum from the as-grown sample is almost exactly same as that from the O₂ annealed sample. This result indicates the mid-gap emission around 515 nm may not be from the Zn-vacancy related states. However, the excitonic peak from the H₂ annealed sample is about 3 times stronger than that from the as-grown sample. The PL peak intensity ratio between the broad peak and the excitonic peak also decreased from 14% to 10% suggesting the H₂ annealing effectively reduces interface/surface states.

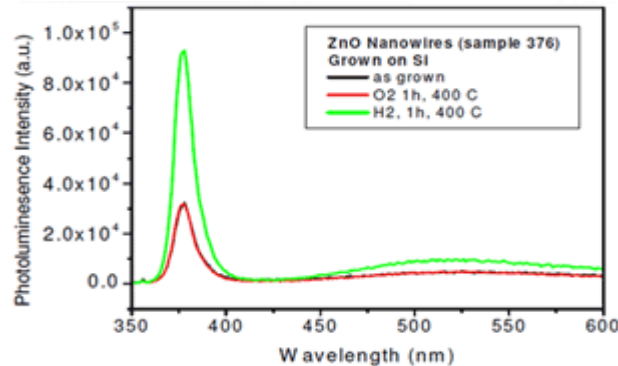


Figure 4: PL spectra at room temperature from the ZnO nanowires grown on Si (100) substrates

The uniformity of ZnO nanowires is studied by scanning PL spectroscopy. Figure 5 shows the excitonic PL intensity of ZnO nanowires grown on a 2" sapphire wafer (0001). The PL intensity is very uniform except a small portion near one of corners. This PL uniformity is expected since the ZnO nanowires growth apparatus described in this paper insures the growth temperature uniformity and optimization reaction gas flow.

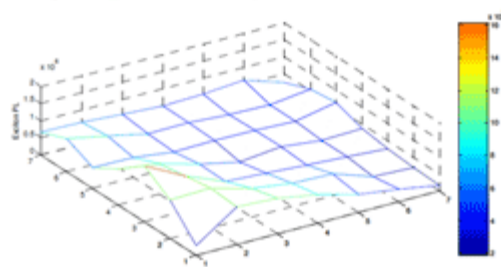


Figure 5: Spatial distribution of PL intensity from excitonic emission of ZnO nanowires grown on a 2" sapphire wafer

CONCLUSION

The traditional method can only get a small temperature uniform zone on the substrate, which is the limit in scaling up ZnO nanowire growth. Therefore, how to achieve uniform ZnO nanowires growth over large area until now becomes a major challenge for many applications. In this work, a solid source heater combined with a three zone furnace was used to achieve large temperature uniformity area on substrate. We successfully controlled the growth temperature uniformity $\pm 5^\circ\text{C}$ at the lower temperature limit (700 to 760 $^\circ\text{C}$) and $\pm 1^\circ\text{C}$ at the higher temperature limit (780 to 820 $^\circ\text{C}$) over a distance of 3 inches at the collection area, which provide uniform environment for ZnO growth. In addition, using a proper length of injector to introduce reaction gases into process tube increased not only the uniformity of ZnO nanowire on the substrate also the efficiency of vapor transport. The SEM images and the PL results show the quality and the good uniformity of ZnO nanowires grown on substrate.

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