

# Method to Convert a Horizontal Furnace to Grow ZnO Nanowires for Gas Sensing by the VLS Method.

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**Abstract**—Zinc oxide (ZnO), II-VI compound semiconductor with a wide band gap (3.4eV), has a stable wurtzite structure with lattice spacing  $a=0.325$  nm and  $c=0.521$ nm. Its properties and potential for applications in photovoltaics, LED's, spin electronics, ultraviolet light emitters, chemical sensors and transparent electronics has attracted intensive research. The objective of this thesis is to fabricate ZnO nanowires on gold coated silicon substrates using the chemical vapor transport (CVT) method. Under a constant flow of Argon gas (200mL/min), the substrates along with a mixture of ZnO and graphite powder are placed in a modified horizontal furnace which uses a 2.54 cm internally mounted quartz tube and are exposed to high temperature (527°C-1000°C) for different growth times. This reaction causes the formation of ZnO nanowires on the substrates. scanning electron microscopy is used to measure the size of the nanowires.

**Keywords**—component; formatting; style; styling; insert (key words)

## I. INTRODUCTION

This paper will demonstrate the use of a standard diffusion furnace with additional quartzware to grow ZnO nanowires. Nanowires have attained a fundamental standing in integrated nano systems and offer fascinating potential for future nanotechnology applications. A one dimensional nanostructure represents the smallest magnitude structure that can effectively transport electrical carriers. Nanowires, tiny rows of semiconductor atoms, personify the best defined class of nanoscale building blocks in a variety of devices in some applications, such as chemical and biological sensors, magnetic devices, photonics, electronics and medical technology. For the synthesis of nanowires, many materials can be used such as Si, GaN, GaP, InP, ZnO [1]. Among all these materials, zinc oxide is a promising material in the growth of nanowires due to its novel properties.

In recent years, nano structured materials grown from II-VI and III-V elements have attracted tremendous interest for their potential applications. Among these nanomaterials, ZnO is one of the most promising which has been recently receiving intensive studies because of its advantageous

properties, including a wide direct band gap (3.37eV), large excitation binding energy (60meV), transparent conductivity and piezoelectricity [2]. Moreover, in biomedical applications ZnO can be used without any coating as it is bio compatible. Because of their high sensitivity to chemical environment, these nanowires are excellent candidates for nanometer scale electronic applications, such as sensors or field emission transistors. ZnO nanowires are also promising candidates for photonic device applications, ultraviolet photo-detectors, light emitting devices and can be used for fabrication of solar cells.

For high purity and quality crystal growth of ZnO, chemical vapor transport (CVT) method is the most suitable one, as ZnO is hard to grow from molten state, due to its high melting point (1977°C) [3]. In CVT, a metal catalyst, which is a second phase material is introduced to limit and direct the crystal growth within a confined area on a specific orientation [4]. This in turn, at high temperatures, forms liquid alloy droplets by absorbing vapor components. Figure 1 shows a schematic of the VLS growth system.

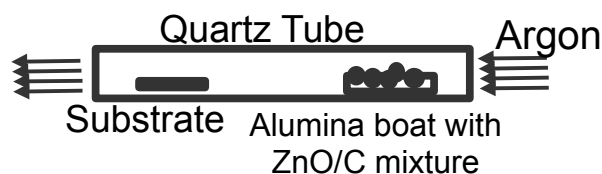


Fig 1. The VLS growth technique. [13].

The alloy is further supersaturated because of either temperature or vapor pressure fluctuation and becomes a solution in which the actual concentration of the components is higher than the equilibrium concentration. At liquid-solid interface, the precipitation of the component is driven to achieve minimum free energy of the alloy system. The position and diameter of the one dimensional structure can be known relating to the size and position of the catalyst at a glance. A liquid phase is limited to the area of the precipitated solid

phase. Since in VLS (Vapor-Liquid-Solid) mechanism, the metal catalyst forms a liquid alloy at high temperature. It is generally used in conjunction with the chemical processes such as chemical vapor deposition, laser ablation, molecular beam epitaxy and carbothermal reduction. Peidong Yang and others developed a simple vapor transport and condensation process for the synthesis of ZnO nanowires via the VLS mechanism [1]. The schematic illustration of the chemical vapor transport and condensation system is shown in Figure 2. Single crystalline silicon and sapphire of different orientations were used as substrates which were then coated with a layer of Au thin film using thermal evaporator.

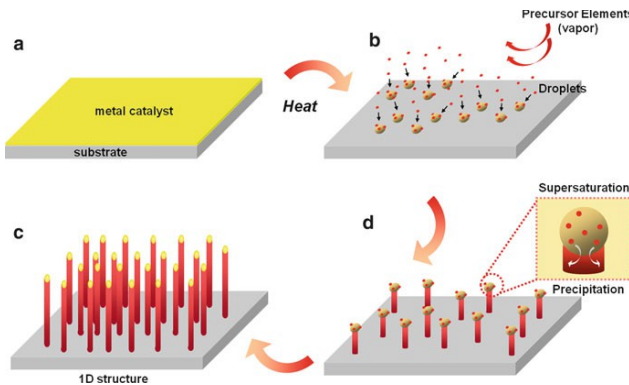


Figure 2: Schematic illustration of chemical vapor transport experimental setup for ZnO nanowire growth [1].

Equal amounts of ZnO powder and graphite powder were ground together and transferred to an alumina boat. The Au-coated substrates and the alumina boat were placed into a small quartz tube. The substrates were typically placed ~5 to 10 cm from the center of the boat. This quartz tube was then placed inside a furnace quartz tube, with the center of the alumina boat positioned at the center of the furnace and the substrates placed downstream of an argon flow. The temperature of the furnace was ramped to ~800°C-1000°C and typically kept at that temperature for ~5-30 minutes under a constant flow of argon (~20-25 sccm). After the furnace was cooled to room temperature, light or dark grey material was found on the surface of the substrates. These ZnO nanowires were then characterized by Scanning electron microscopy (SEM), X ray Diffraction (XRD) and transmission electron microscopy (TEM). The results showed that the diameters of the nanowires range from 20-120nm, their lengths are 5-20 μm, similar XRD patterns indicating high crystallinity of nanowires.

Owing to the wide band gap of 3.37 eV and the large excitation binding energy of 60 meV at room temperature, ZnO has long been recognized as an ideal material in many applications. Most nano-optoelectronic and nano-electronic devices, such as nano-LEDs, nanogenerators and nanopiezotronic devices [5-11], are built up of p-type ZnO nanowires. Many researchers showed interest in growing p-type ZnO nanowires but least research work was done on n-type ZnO nanowires. Objective of this project is to grow p-type and n-type ZnO nanowires at low temperatures. For high purity

and quality crystal growth of ZnO, chemical vapor transport (CVT) method is the most suitable one, as ZnO is hard to grow from molten state, due to its high melting point (1977°C) [6]. In such a process, ZnO powder is mixed with graphite powder as source material. At about 800°C-1100°C, graphite reduces ZnO to form Zn and CO vapors. Zn and CO later react and result in ZnO nanocrystals. The advantages of this method lie in that the existence of graphite significantly lowers the decomposition temperature of ZnO.

## II. EXPERIMENTAL PROCEDURE

The growth of ZnO nanowires was carried out in a tube furnace called the Lindbergh furnace. A horizontal 11.3 cm diameter quartz tube with one side open, was placed inside the Lindbergh furnace. The length of the tube was measured to be 1.34 m long, where the center of the tube is around 0.6 m and 0.635 m from the edge of the tube. The experiment was performed in a 2.54 cm quartz tube which was placed inside the large quartz tube.

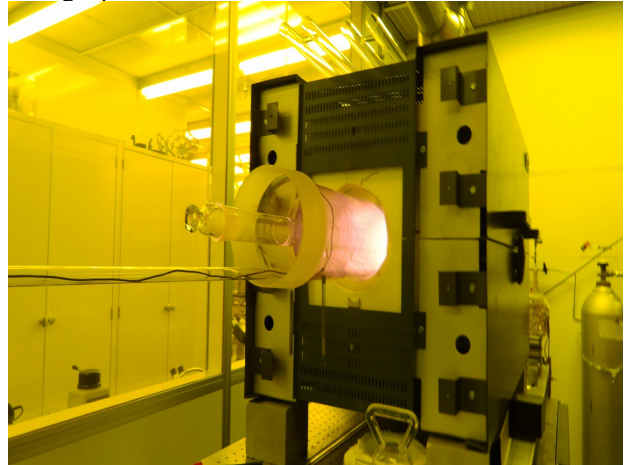


Fig. 3. Lindbergh Furnace used to produce VLS ZnO nanowires.

The Lindbergh furnace is a three zone furnace, in which the center has the highest temperature and the temperature gradually decreases towards the ends [7]. The furnace was profiled multiple times at different temperatures. The furnace was set to a temperature of 1000°C, but the actual temperature was less than the set temperature. Hence, profiling the furnace using a thermocouple made it easy to understand its temperature settings at different points. An alumina crucible containing ZnO and graphite mixture was placed inside the 1 inch quartz tube at a position corresponding to the furnace center. According to the thermocouple, the temperature at the center of the furnace was 927°C where the source was placed.

A clean p type silicon (100) wafer was diced into 2.5 cm X 1.25 cm pieces. Before depositing gold, these parts were cleaned in Nanostrip®. The solution was heated to 60°C and the parts were cleaned for 10 minutes. The parts were then rinsed in a dump rinse for ten cycles with 15 MΩ deionized water. The final step was to spin dry the parts. Gold was deposited on the cleaned silicon substrates using the Temescal BJD deposition system in the Microelectronics Research and

Development Laboratory. The thicknesses of gold deposited on the substrates were 1 nm, 3 nm, 6 nm, 9 nm and 12 nm. The gold coated substrate was placed at the left corner of the furnace, downstream of an argon flow. The temperature of the furnace was ramped up to 1000°C. Initially, a set of experiments was carried out without the ZnO and graphite powder. The substrate was placed at a point where the temperature was 783°C. A constant flow of argon gas at 200 ml/min was supplied into the tube. The process was continued for different growth times (5 minutes, 30 minutes and 1 hour).

TABLE 1. P-TYPE SUBSTRATES WITHOUT ZnO POWDER.

Substrate Au Coating (nm)	5min	30min	1hour
1	X	X	X
3	X	X	X
6	X	X	X
9	X	X	X
12	X	X	X

A mixture of high purity ZnO powder and graphite taken in equal measure were ground together and loaded in an alumina crucible. The alumina crucible, with the mixture in it, was placed at the center of the furnace. According to the thermocouple, the temperature at the center was around 927°C. Initially the substrates were typically placed approximately 34.3 cm away from the center of furnace. The substrate region was at 783°C. A constant flow of argon gas at 200 ml/min was supplied into the tube. The process was continued for different time periods (5 minutes, 30 minutes and 1 hour), and then the furnace was cooled down to room temperature.

The equation for the dissociation reaction is as is as follows:

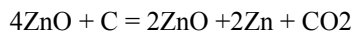


TABLE 2. P-TYPE SUBSTRATES WITH ZnO POWDER AT 783°C SUBSTRATE TEMPERATURE

Substrate Au Coating (nm)	5min	30min	1hour
1	X	X	X
3	X	X	X
6	X	X	X
9	X	X	X
12	X	X	X

As the nanostructures were clearly seen on 1 nm gold deposited substrates, the experiment was repeated. These experiments yielded the same results as before, confirming the correct conditions for the nanowires to grow.

TABLE 3. P-TYPE SUBSTRATES WITH ZnO POWDER AT DIFFERENT SUBSTRATE TEMPERATURE AND THEIR CORRESPONDING GROWTH TIMINGS.

Substrate Au Coating (nm)	527°C			627°C		660°C	690°C
	1 hr	2 hr	4 hr	1 hr	2 hr	1 hr	1 hr
1	✓	✓	✓	✓		✓	✓
3	✓	✓		✓	✓		
6	✓			✓		✓	✓
9	✓			✓		✓	
12	✓			✓		✓	

### III. RESULTS AND OBSERVATIONS

The intent of this research work was to observe the growth of nanowires at different conditions and confirm these to be optimal for the growth. Initial data was collected by conducting the experiment without placing the zinc oxide powder in the quartz tube. Figure 3 corresponds to SEM images of P-Si with 60Å gold coating, processed without ZnO powder at 783°C for 1 hour. It was observed that, when these substrates are exposed to high temperature, the formation of gold islands occurs. These set of experiments i.e., without ZnO powder acts as a baseline for the research.

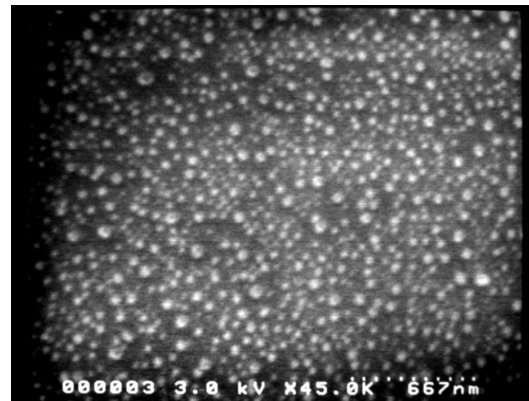


Fig. 3. SEM result of P-Si (60Å Au) without ZnO powder at 783°C for 1 hour at 45000 magnification

There was no growth observed on the samples processed at temperatures 727°C or 783°C. The reason for this might be the substrate temperature (783°C), at which, the metal catalyst i.e., gold, diffused too quickly into the silicon substrate. The SEM images of these substrates show the formation of gold islands

without any zinc in it. Figures 4 and 5 shows the SEM images of P-Si 6 nm Au and 9 nm Au substrates respectively at 783°C temperature. These were similar to the substrates processed without ZnO powder.

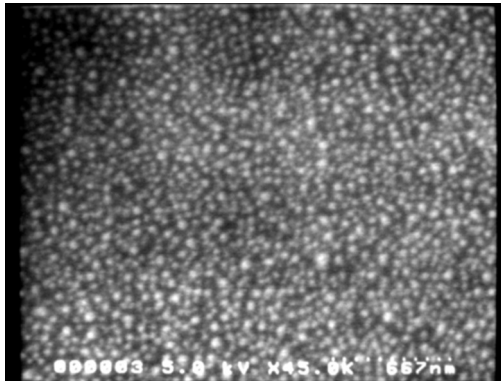


Fig. 4. SEM result of P-Si (60Å Au) at 783C for 1 hour at 45K magnification.

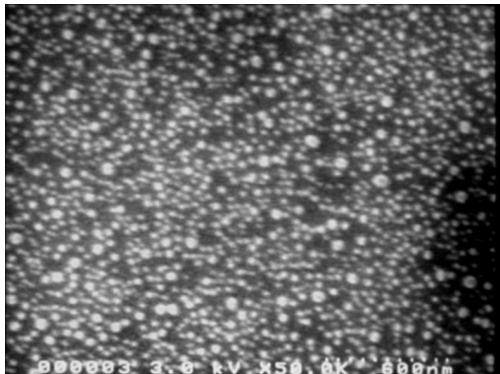


Fig. 5. SEM result of P-Si (90Å Au) at 783C for 1 hour at 50K magnification

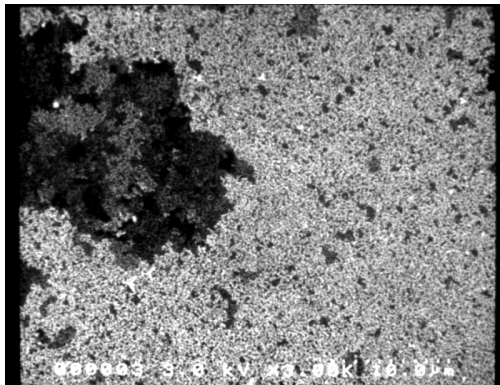


Fig. 6. SEM result of P-Si (1 nm Au) at 627C for 1 hour at 3kX magnification

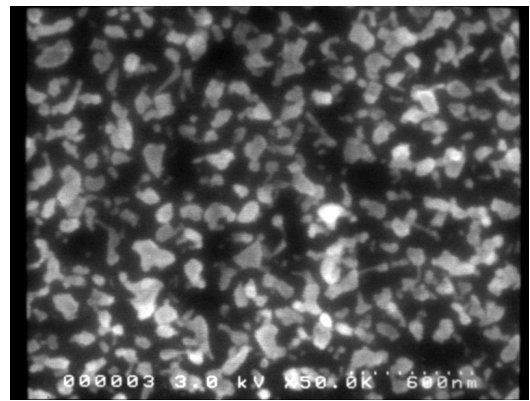


Fig. 7. SEM result of P-Si (1 nm Au) at 627C for 1 hour at 50 KX magnification

At 727°C, it was observed that the hexagonal structures started growing. Also, when the Argon gas pressure was reduced to 25 mL/min, the growth of nanowires was not observed. Hence to know the exact growth conditions for super saturation, three substrates were placed at three different temperatures i.e. 527°C, 627°C and 727°C for 200mL/min gas pressure. At 627°C temperature, a slight growth with very less density was observed. Figures 6 and 7 correspond to SEM images of P-Si (1 nm Au) at 627°C at different magnifications.

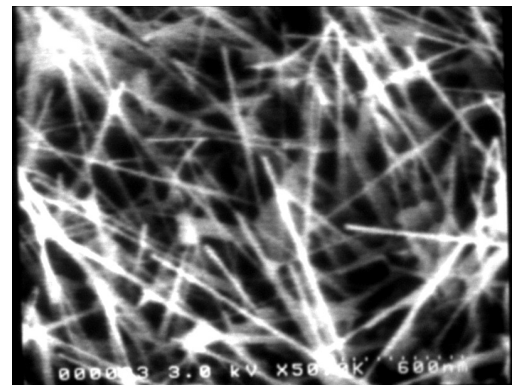


Fig. 7. SEM image of P-Si (10Å Au) at 527C for 4 hours at 50KX magnification.

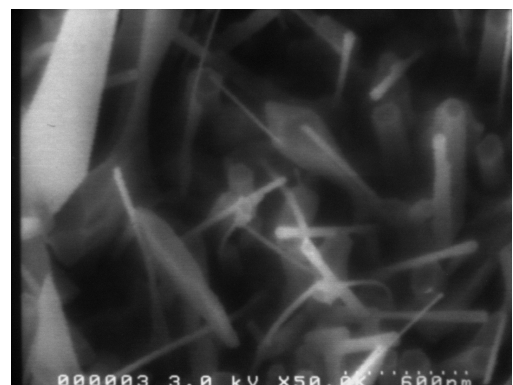


Fig. 8. SEM image of P-Si (10Å Au) at 527C for 2 hours at 50000 magnification.

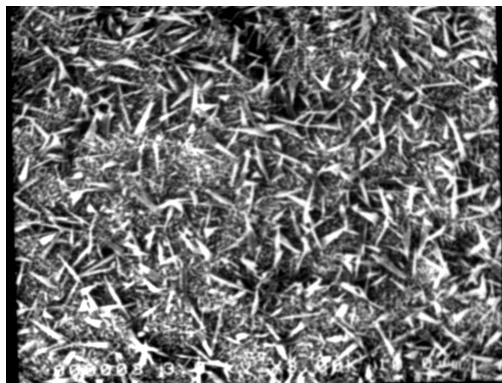


Fig. 9. SEM image of P-Si (1 nm Au) at 527°C for 4 hours at 3kX magnification.

At growth temperature 527°C, on 1 nm gold coated substrate, we observed growth of ZnO nanowires. Figures 7, 8, 9 and 10 belong to the SEM images of the substrates processed for 4 hours and 2 hours with different magnification. It was observed that the density of the wires has been increased as the growth time increases. As the nanostructures were clearly seen, the experiment was repeated. These experiments yielded the same results as before, confirming the correct conditions for the nanowires to grow.

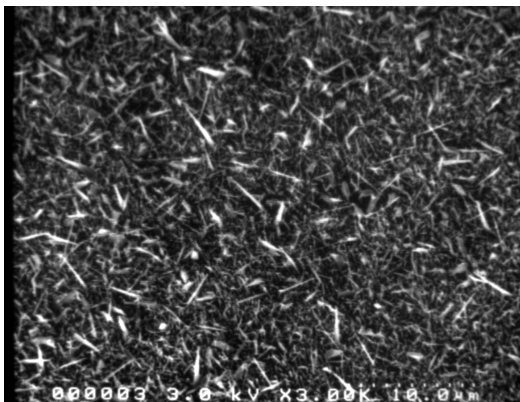


Fig. 10. SEM image of P-Si (1 nm Au) at 527°C for 2 hours at 3KX magnification.

for 4 hours and 2 hours with different magnification. It was observed that the density of the wires has been increased as the growth time increases. As the nanostructures were clearly seen, the experiment was repeated. These experiments yielded the same results as before, confirming the correct conditions for the nanowires to grow. Further work will include UV-visible spectroscopy to determine the electronic type of the ZnO nanowires.

#### IV. CONCLUSIONS

This experiment demonstrates that ZnO nanowires can be grown using VLS growth techniques using a standard horizontal diffusion system. Careful characterization of the

growth tube allows for adjusting the temperature profile which in turn allows for super saturation of the argon carrier gas. The higher substrate temperatures and the tube temperature does not allow the ZnO to come out of solution. The VLS method requires that the AuSi nanodot act as a continuous catalyst for the epitaxial growth reaction. By using a smaller inner tube (2.54 cm), the process could be confined to a smaller volume. The substrate temperature that was able to demonstrate the growth of nanowires was 527°C, a little over half of the initial temperature. The temperature distribution on the substrate still controlled the distribution of nanowires, causing only a fraction of the substrate with a coating of wire like structures. Future work is focusing on redesigning the deposition system as a two stage furnace.

#### V. ACKNOWLEDGMENT

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