Direct growth of ZnO tetrapod on glass substrate by Chemical Vapor Deposition Technique

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Abstract. This research demonstrates the growth of ZnO tetrapod structure on glass substrate for different types of flow gas and at different growth temperatures. The study on the morphological structure and electrical properties of ZnO thin film growth by Chemical Vapour Deposition (CVD) technique showed that the optimum growth temperature was obtained at 750˚C with ZnO nanotetrapod morphological structure. Introducing Nitrogen gas flow during the growth process exhibited leg-to-leg linking ZnO tetrapods morphology. The electrical properties of ZnO tetrapods film were measured by using two point probes and it shows that, the sample growth in Ar and O\textsubscript{2} atmosphere have better I-V characteristic.

1. Introduction
Zinc oxide (ZnO) is known has a good characteristic on electrical properties and can used for higher temperature condition, good transparency and high electron mobility [1-3]. In addition, ZnO are one of the several metal oxide that can be used as a fabrication for the others generation of optoelectronic device and display device. ZnO has a larger bandgap of 3.37 eV. The ultraviolet light emitting diode and lasers are attracted with characteristic of zinc because it has a good wide band gap [4]. ZnO can growth in various types of morphology structure such as nanowires, nanorods, nanobelts, nanosrings, nanostars, nanotube, nanopropellers and others. ZnO nanostructure can be growth from several deposition techniques such as vacuum, thermal evaporation, dip-coating, sol gel and other [5]. The chemical vapour deposition (CVD) has been chosen in this experiment due to its simple preparation and low cost deposition method. Different gas flow, growth time and annealing time may affect the properties of ZnO either in morphology or electrical characteristic. Thus, in this experiment, it is essential to study the effect of different gas flow on the growth of ZnO tetrapod as promising films for any electronic applications.

The structural properties of ZnO have been observed using field-emission scanning electron microscopy (FESEM) and the electrical properties was characterized using I-V measurement.
2. Experimental details
The ZnO tetrapods were prepared by thermal evaporation of 2g Zn powder with a purity of 99.9%. Glass slides were used as the substrate and were cut in the size of 2.5cm x 2.5cm. Prior to the experiment, glass substrates were cleaned using acetone, methanol and deionized water. Glass substrates were immersed in a beaker with acetone and followed by methanol and deionized water, respectively. The ultrasonic machine was set to 45°C and takes 15 minutes for each solution. The cleaning process is conducted because to avoid from nanoparticles or contamination of small structure form on the surface of the glass substrate. Small particle that adhere on the glass surface are feared can scratch the surface during the cleaning process. If any scratches formed on the glass surface, it can effect on surface morphology of the sample.

The Chemical Vapor Deposition (CVD) has two furnaces. The growth temperature at the first furnace was heated at 650 ˚C, 750 ˚C and 850 ˚C, individually. Second furnace where the substrate was placed was kept at 500 ˚C for all growth temperature. Before the growth process, the tube was cleaned by allows Argon gas to flow in the rate of 68 sccm for 15 mins to eliminate unwanted particles. Once the furnace reach the desired temperature, Argon gas was maintained flow for 30 mins then followed by Oxygen gas flow at 5 sccm for another 30 mins. At this point, Argon and Oxygen was mixed in the tube. The evaporated Zn vapor was reacted with oxygen in air to form the tetrapod-shaped ZnO crystals. After 30 mins, the furnace was turned off and cooled to room temperature. Then, the samples were collected for characterization. This method was repeated for samples with Nitrogen gas flow at 13 sccm.

The morphology of as-grown and annealed samples was observed by field-emission scanning electron microscopy (FE-SEM). Energy dispersive X-Ray (EDX) was used to analyze the element in the fabricated film. The electrical properties of the samples were characterized by two-point probe solar simulator. Gold was sputtered on the sample as the metal contact.

3. Results and Discussion
The density of as-grown and annealed ZnO tetrapods structure and the electrical properties were investigated for all growth temperature. The flow of nitrogen gas during the growth process shows effect on the density of the ZnO tetrapods.

3.1. Surface Morphology
The FESEM images of direct-grown ZnO tetrapods growth at 650 ˚C, 750 ˚C and 850 ˚C on glass substrate are shown in Figure 1 (a)-(c). All growth temperatures show formation of ZnO tetrapod on the glass substrate. The density of ZnO tetrapods covers most of the surface area of the glass substrate. The density at 650 ˚C is less than ZnO tetrapod during growth at 850 ˚C. The evaporation of ZnO powder is increasing when higher growth temperature is used. Inset figure in Figure 1 (a) shows the ZnO tetrapods with an average length of 1.35 µm and 0.08 µm width. When the growth temperature was set to 750 ˚C, ZnO tetrapods width and length shows an increase in average of 0.15 µm and 1.69 µm, respectively as shown in inset figure of Figure 1 (b). While, inset figure of Figure 1 (c) shows the higher the growth temperature, the longer length of ZnO tetrapods but no changes on the width of ZnO tetrapods. However, higher growth temperature tends to bend the branch of ZnO tetrapod which could increase the resistance due to the bending structures. ZnO tetrapods growth at 650 ˚C shows a large boundaries between each other compared to 750 ˚C. In the next steps, we introduce N2 flow during the growth process to observe the effect on ZnO tetrapod at the same growth temperatures.
3.2. Effect of Nitrogen on ZnO tetrapods

Besides Oxygen and Argon flow, we introduced 13 sccm of N₂ flow rate during ZnO tetrapod growth. From the FESEM images as shown in Figure 2 (a)-(c) for 650 °C, 750 °C and 850 °C, respectively, Nitrogen-rich atmosphere shows abundant of ZnO tetrapods compared to only Argon and Oxygen gas. Inset figures shows higher magnification of the tetrapods. Morphology analyses showed that, nitrogen used in this process leads to an enhancement of ZnO tetrapod densification [6]. Optimum density is required to create a path for electron movements. Thus, higher density of ZnO tetrapod growth in nitrogen ambient increases the surface area which is useful to apply on any application that needs higher sensitivity such as sensors.

On the upper region, we observed leg-to-leg linking of ZnO tetrapods as shown in Figure 3. The inset figure shows higher magnification clearly shows the linking between one leg with another tetrapods leg. The morphology of linked legs is due to the existing of N₂ in the quartz tube during the growth process which increases the pressure and resulting ultrahigh supersaturation condition inside the tube. The high supersaturation condition results to an increase in the nucleation of ZnO tetrapods [7]. Formation of leg-to-leg ZnO tetrapods on the upper region can be explained due to high vapor pressure in the tube which induced more vapor accumulated on top of the tube and leading to condensation of leg-to-leg linking ZnO tetrapods.

Figure 1: ZnO tetrapod growth at (a) 650 °C (b) 750 °C and (c) 850 °C
Figure 2: ZnO tetrapod growth under mixing of N$_2$, Ar and O$_2$ flow at (a) 650 °C (b) 750 °C and (c) 850 °C

Figure 3: Leg-to-leg ZnO tetrapods on the upper region of ZnO film. Inset figure: High magnification of ZnO tetrapods leg-to-leg linking
Figure 4 shows EDX pattern of direct growth ZnO tetrapods on glass substrate. The EDX data reveals that all the samples are composed of Zn and O elements. The Si element observed from the EDX data is believed from the glass substrate.

![EDX pattern of ZnO tetrapods](image)

Figure 4: EDX pattern of ZnO tetrapods

3.3. Electrical properties

Figure 5 shows the I-V characteristic of ZnO tetrapods samples prepared under N₂ atmosphere and without N₂ atmosphere. From the I-V curve it shows that, sample prepared with N₂ flow resulting in lower conductivity. The reasons can be assume due to higher density by stacking morphology and leg-to-leg linking might increase the resistance throughout the path.

![I-V characteristic of ZnO tetrapods](image)

Figure 5: Electrical characteristic of ZnO tetrapods
4. Conclusions
Based from all growth temperatures, 750 °C shows the optimum growth temperature for both atmosphere conditions, with and without N₂. Higher temperature tends to bend the leg of the ZnO tetrapods thus potential to increase the resistance. Based from the morphology, lower growth temperature shows isolated ZnO tetrapods which lead to the higher needs of external voltage in order to excite the movement of electrons. The leg-to-leg linking ZnO tetrapods is beneficial for electronic, photonic, opto-electronic, and sensing applications due to higher surface area.

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