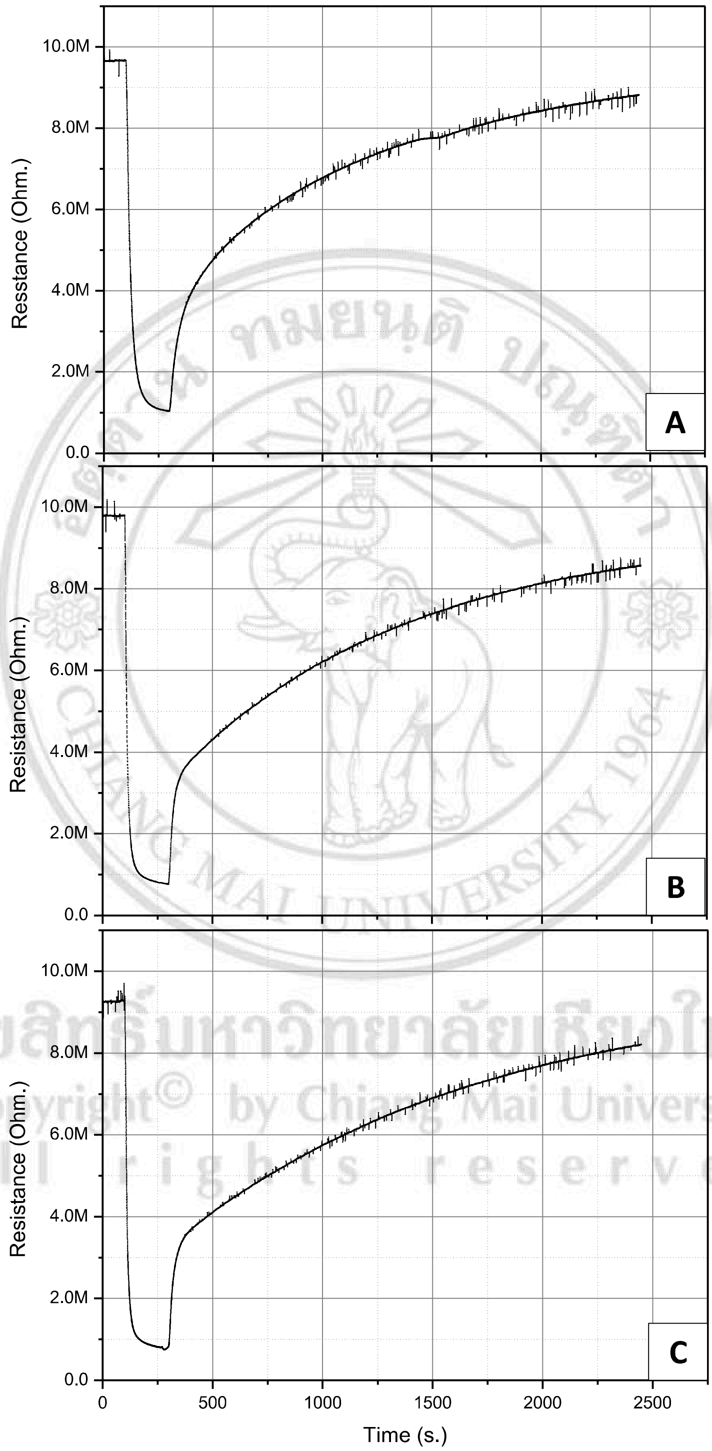
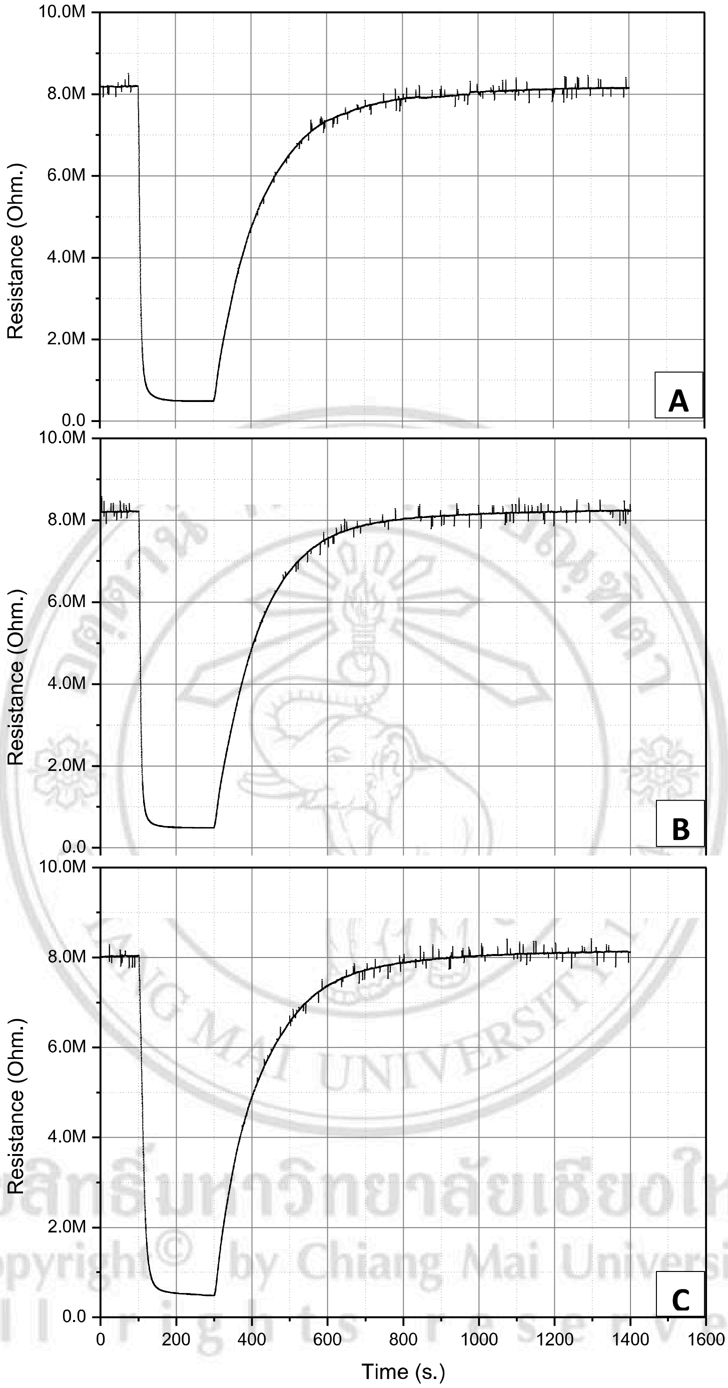
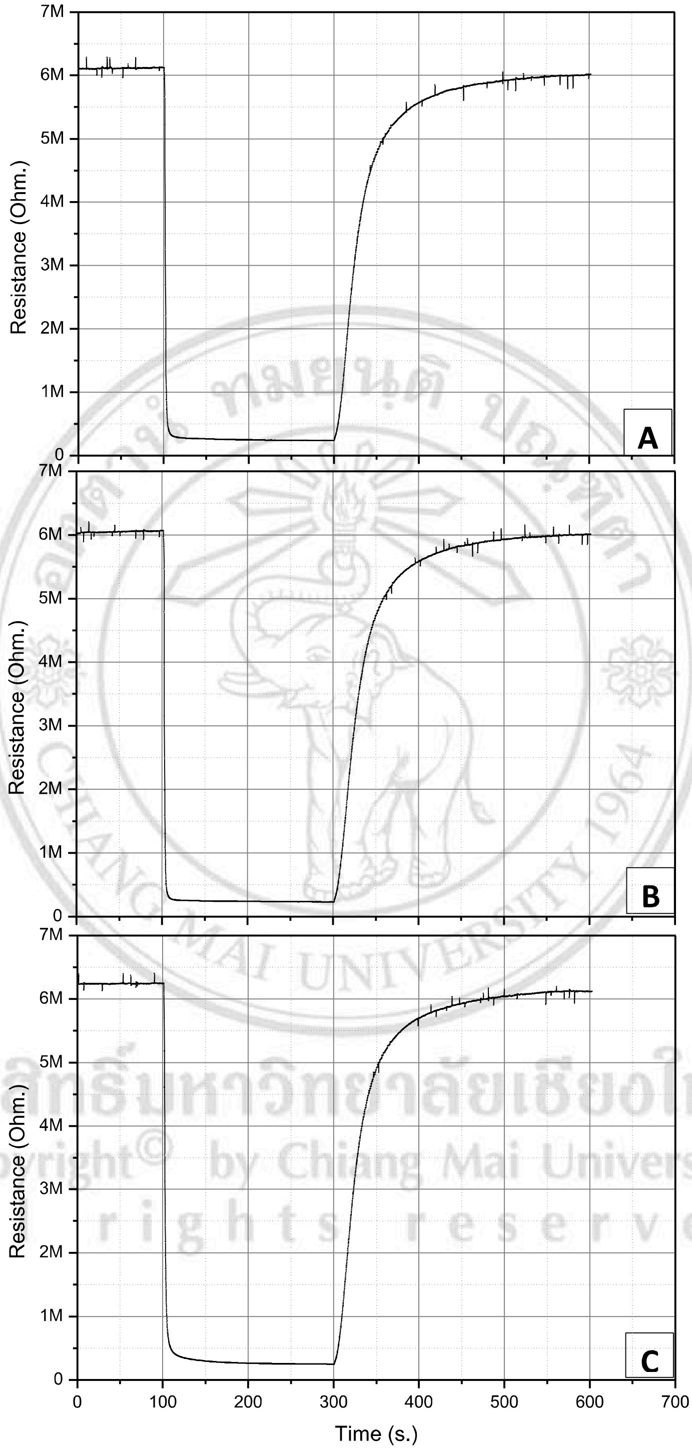
Appendix A



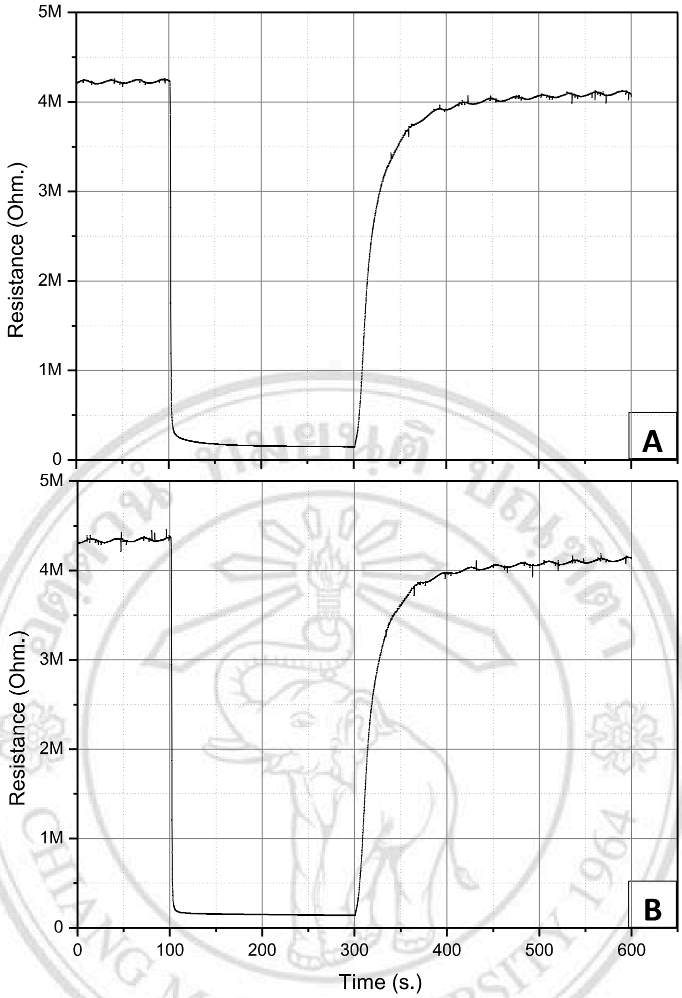
Gas response at 350°C of operating temperature : Sample A-C



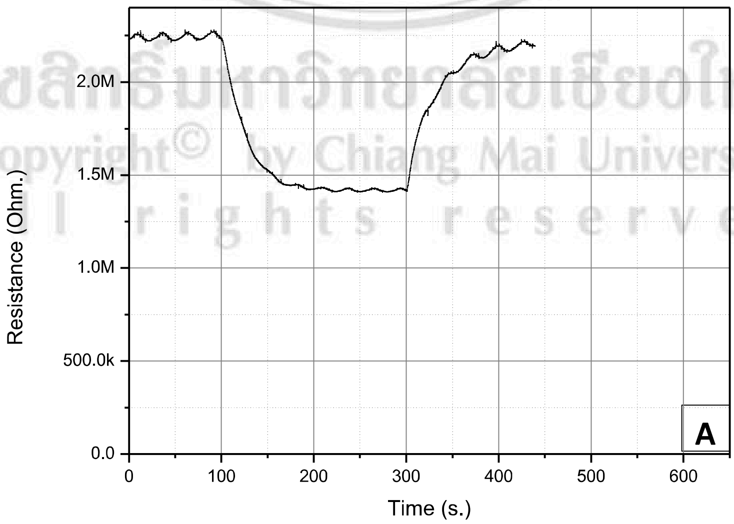
Gas response at 400°C of operating temperature : Sample A-C



Gas response at 450°C of operating temperature : Sample A-C



Gas response at 500°C of operating temperature : Sample A and B



Gas response at 550°C of operating temperature : Sample A

Appendix B

Paper I

THAI JOURNAL OF PHYSICS, SERIES 9, (2014)

Synthesis and Characterization of Vertically Aligned ZnO Nanowires by Chemical Vapor Deposition

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Vertically aligned ZnO nanowires (VA-ZnO-NWs) were successfully synthesized by chemical vapor deposition technique (CVD) on coated glass slide substrate assisted growth under acetone ambient. Firstly, the glass substrate was coated with zinc acetate dehydrate to form seed layer. The coated glass substrate would then be set in tube furnace. The growth of the VA-ZnO-NWs on the seed layer was controlled under different temperatures. The growth temperature of 400-550°C was varied by changing the substrate position in the chemical vapor deposition furnace. The VA-ZnO-NWs were finally characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM) to expose crystal structure and structural morphology. The results show that the VA-ZnO-NWs were single crystalline with hexagonal wurtzite structure and the diameter of vertically aligned ZnO nanowires was in a range from 56.3 to 261.3 nm.

Keywords: ZnO, Chemical Vapor Deposition, Nanowires, CVD

1. INTRODUCTION

Recently, metal-oxide semiconductors have been reported as attentive materials for gas sensor due to their extraordinary properties. In addition, these materials also show the great potential applications for dye synthesized solar cell. As a result, they have been widely investigated, and many works have been reported on TiO_2[1], ZnO[1, 5, 3], WO_3[1], SnO_2[1], In_2O_3[1], etc. Among of these candidates, ZnO is one of the most promising one because of its wide-band-gap with a direct band-gap of 3.37 eV and a high exciton binding energy of 60 meV.

Nowadays, many researchers play their attention on nanostructure materials since these nanostructures have a higher surface-to-volume ratio compared with those bulk and thin film. Because of enormous surface area, nanostructures can absorb more gas molecules which directly relate to sensitivity of the sensor. Therefore, many techniques have been developed in order to synthesize the nanostructures to achieve high surface area. Pulse laser deposition (PLD), aqueous solution method and thermal oxidation technique have been applied to produce one-dimensional ZnO nanostructures. Of these various methods available for synthesizing nanowires, chemical vapor deposition (CVD) technique with alumina substrates present a particular cost-effective and high-quality equilibrium process for the growth of 1D ZnO nanostructure. [1, 2, 3, 5, 8]

In this work, we have used chemical vapor deposition (CVD) technique to prepare vertically aligned ZnO-nanowires (VA-ZnO-NWs) on coated glass slide substrate in presence of acetone vapor. This technique has benefits on low production cost, easily capable and high crystal quality. The obtained VA-ZnO-NWs were then characterized for crystal structure and structural morphology.

2. EXPERIMENT

Glass slide substrate was cleaned in order to remove surface contamination by detergent, DI water and acetone, respectively. Next, drop coating technique was applied with 5 mM. solution of zinc acetate dihydrate in acetone for 5 time to ensure the solution fully cover substrate. After treating, the substrate was then used for growing VA-ZnO-NWs. The VA-ZnO-NWs arrays were grown in tube furnace by chemical vapor deposition (CVD) technique as shown in Figure.1

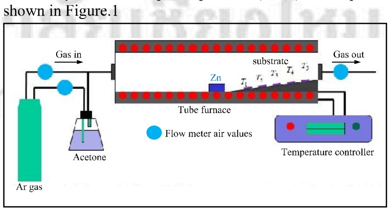

FIGURE 1. Schematic illustration of the chemical vapor deposition (CVD) technique based on Zn seeding layers and local temperatures on the substrate under acetone ambient.

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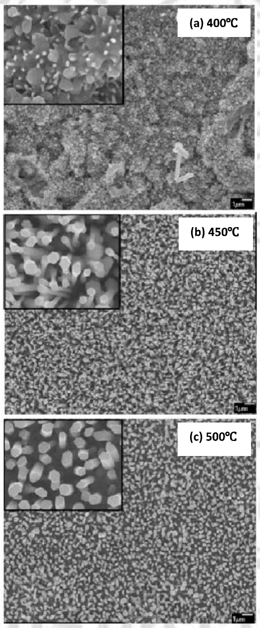
In this process, Zn powder will be used as a source, prepared in ceramic boat, placed at the center of tube furnace (around 850°C). Glass slide substrate with Zn seeding layer was placed at growth zone, temperature in range of 400 – 550°C position under ambient Ar gas with a flow rate of 1 L/min in the tube furnace for 7 minutes in order to get rid of remaining O_2 in the tube furnace, the valves were closed for preventing ZnO vapor leakage out of the system during ionizing. At the temperature heating up to 850°C, acetone flow with a rate of 5 sccm, mixed with Ar gas of 0.5 L/min for 15 min. After that, valves were closed for the oxidation reaction between ionized Zn and O_2 for 30 min. Then, the valves were opened and Ar gas of 1 L/min was released for 10 min to push out gas in tube furnace before turning off system.

Crystal structure of the VA-ZnO-NWs was evaluated by X-ray diffractometry (XRD) and morphology was measured by scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSIONS

FE-SEM images of the VA-ZnO-NWs on glass substrate with zinc acetate dehydrate seeding layer, grown at deposition temperature 400°C-550°C under acetone atmosphere are shown in Figure. 2.



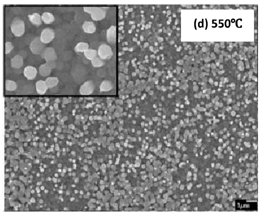


FIGURE 2. FE-SEM images of the VA-ZnO-NWs at temperature of (a) 400°C, (b) 450°C, (c) 500°C, and (d) 550°C, respectively

This figure demonstrated that the density of ZnO nanowires increases while temperature rises up. Furthermore, the uniformity of ZnO nanowires in each deposition temperature also increases. This result conforms to a work by S. Choopun et.al. [1] The density of ZnO nanowires is represented by nuclei probability given by [1]

$$P_N = \exp(-\Delta G_N^* / k_B T), \qquad (1)$$

where P_N is the nuclei probability, ΔG_N^* is the maximum energy barrier, k_B is Boltzmann constant and T is growth temperature. It can be seen that the probability increases when temperature increases. Deposition temperature affect oxidization in forming ZnO-nanowires. The nanowires are uniformity and well aligned on the glass substrate at deposition temperature 550°C, 500°C and 450°C while at deposition temperature 400°C, FE-SEM reveals the low density of ZnO nanowires due to deposition temperature below melting point of Zn. Thereby, the Zn was ionized lower than other condition.

Temperature (°C)	Average diameter (nm.)
400	56
450	174
500	261
550	254

Table. 1 Average diameter of the VA-ZnO-NWs

As a result, it can be seen that the diameter of ZnO nanowires increase while deposition temperature increase as shown in Table 1. Because of temperature effect, nuclei probability governed to increase and ZnO nuclei. will be occurred plentifully. Moreover, ZnO nuclei will fuse and connect nearby nuclei, consequently forming larger nuclei.

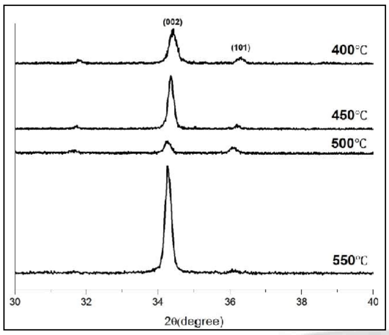


FIGURE 3. XRD pattern of the VA-ZnO-NWs at different temperatures

XRD patterns were shown in Figure 3. The XRD data was found to be well in agreement with JCPDS file no. 89-13971 corresponding to hexagonal wurtzite ZnO nanowires with lattice parameter $a = 3.253$ Å and $c = 5.213$ Å. It demonstrated a strongly preferential orientation in the c-axis, indicating (002) and (101) directions and suggests good crystallinity. After ZnO nanowires were formed, growth direction will be designed by Eq. (1) which is minimization surface energy. ZnO nanowires will grow up on the facet that is the lowest surface energy. It can be seen that preference growth direction is (002) due to (002) is the lowest surface energy (around 1.2 J/m^2)[1].

4. CONCLUSION

In summary, vertically aligned ZnO nanowires (VA-ZnO-NWs) were synthesized on coated glass slide substrate by a chemical vapor deposition technique. The formation of the VA-ZnO-NWs could be supported by Zn seeding layer and local temperature on the substrate at growth temperature of 400–550ºC under acetone ambient. The VA-ZnO-NWs grew on top of Zn seeding layers, forming a 1D quantum wire with diameters ranging from 56.3 to 261.3 nm. The VA-ZnO-NWs exhibited single crystalline with hexagonal wurtzite structure. With further benefits, this technique may be applied to produce other metal oxide semiconductors as vertically aligned nanowires in the future.

ACKNOWLEDGMENTS

The author would like to acknowledge the financial support via Thailand Center of Excellence in Physics and The Graduate School, Chiang Mai University, Thailand. Besides, I would like to thank the members of Applied Physics Research Laboratory for giving me the useful suggestion for research.

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