Using non-continuous gold film as the seed layer for developing zinc oxide nanowire array

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Abstract. This study aims to discuss the grown morphology and current generation of ZnO nanowire array developed from non-continuous Au thin film as the seed and compare the results with the nanowire array from ZnO thin film as the seed layer. The zinc nitrate hexahydrate and hexamethylenetetramine used as the reaction solution and the hydrothermal process with process temperature less than 95°C are applied. It is revealed that ZnO nanowires developed with non-continuous Au film as the seed appear sparser density, present better crystallization direction (002) and higher collimation. The effect of concentration of reaction solution on the diameter, length and distribution of nanowires is reported. The electron back scattering diffraction technique confirms each grown wire is a single crystal from the bottom to top. The ZnO nanowires with piezoelectric property are measured with the conductive atomic force microscope system. The result shows that single ZnO nanowire could generate more than 800 pA current when being bent.

1. Introduction
Tian et al. opened a new era and synthesized zinc oxide nano-structure on a substrate with seed in 2002 [1]. In the same year, Boyle et al. in UK synthesized Zinc Oxide micro rods with a two-phase process [2]. The zinc oxide seed layer was first prepared at the first phase and zinc oxide micro rods were developed at the second phase. Yang et al. further developed highly aligned ZnO nanowires on the silicon substrate with the two-phase technology in 2004 [3]. Wang and Song utilized the characteristics of aligned ZnO nanowires and successfully converted mechanical energy into electric energy under nanoscale [4]. The thick and dense ZnO nanowire arrays with random preferable orientation were documented in the references [1-4].

Spin coating [5] and ZnO sputtering were used in this laboratory for preparing seed layer and successfully synthesized ZnO nanowires with distinct density and appearance by using aqueous solution with different concentrations. The piezoelectric test was further preceded. Nonetheless, it was discovered that ZnO nanowires developed with low concentration appeared to have worse collimation and that the nanowires could not easily generate power in the entangled and less alignment condition. Under high concentration, the developed nanowires presented excellent collimation, but excessive concentration resulted in difficulty deformation because of the intimate rod contact. The measured voltage/current characteristics therefore were not satisfactory [5]. The purpose of the study is to generate the nanowire arrays with controllable concentration and wire density of the nanowire array as a proposal to introduce more electric current. The gold film was used as the seed layer at the first
phase in order to develop aligned ZnO nanowires with lower density was first proposed by Wang at al. but no electric performance was measured [6]. In order to enhance the piezoelectric efficiency, Lee et al. [7] produced a device using MEMS technology by covering ZnO nanowires arrays with P-type P3HT material and successfully applied ZnO nanowires to piezoelectric element to enhance the piezoelectricity.

2. Experiment method and step
The ZnO nanowire arrays were prepared by a two-phase process. The seed layers were coated on the silicon substrate using the sputtering system and the wire arrays were developed in the solutions with different concentrations using the hydrothermal technology. The silicon wafers were cleaned in the ultrasonic baths by sequential dipping and rinsing in the acetone, DI water, isopropyl alcohol, DI water, each step for 10 minutes to remove the dusts and grease in the surface and were dried by the blown N2. The gold film of 10 nm thickness was deposited on substrate as seed layer using the DC sputtering system with working pressure of 5.7x10⁻² torr and deposition rate of approximate 0.8 Å/s. The ZnO film of 10 nm thickness was prepared using RF sputtering system with simultaneous introduction of 25 sccm argon flow rate and 20 sccm oxygen flow rate. The reaction solutions, Zn(NO₃)₂ · 6H₂O and C₆H₁₂N₄ (HMTA) with the different concentrations, were prepared separately and then mixed and poured into a Teflon container to become a solution of predetermined concentration. The Teflon container with solution was sealed and maintained in a furnace with set temperature of 90°C for the determined time.

The morphology of the obtained ZnO nanowire array was examined by a scanned electron microscope. Microstructural analysis was performed using the X-ray diffractometry with a Cu-Kα ray. The crystal identification of single rod was observed by electron backscattering diffractometry. The bending induced current of the prepared rods was measured using a conductive atomic force microscope with a metal Pt-coated probe tip.

3. Result and discussion

3.1. Comparison of nanowire arrays developed with Au and zinc oxide as seed layers
The initial seed layer exhibits great influence on the development of ZnO nanowire arrays with hydrothermal method. The reaction solution with the concentration 0.07 M, is then added for developing ZnO nanowires. The reaction temperature is 90°C and the development time is 5 hrs. Figures 1a and 1b are the top surface SEM of nanowires developing on Au seed layer and ZnO seed layer, respectively. The ZnO nanowires present hexagonal prism on the top end of rod, conforming to ZnO wurtzite hexagonal structure. The nanowires developed on the ZnO seed layer are tighter, and the initially developed nanowires appear to be interlocked; besides, merely initially developed aligned nanowires could develop upwards. The ZnO nanowires show large differences in density; ZnO nanowires developed from Au seed appear more spaced, while those developed from ZnO seed are
tighter. The bottom substrate cannot be viewed from the top of the array developed on ZnO seed layer substrate.

Figure 2 shows the X-ray diffraction pattern of ZnO nanowires developed from Au seed layer and ZnO seed layer. It is obvious that ZnO nanowires developed from both seed layers grow along with the preferred orientation (002) crystal plane. The crystallization direction of nanowires developed from Au seed is more consistent, while those developed from ZnO seed layer would exist in (102) and (110) directions with inconsistent crystallization direction.

![XRD pattern of ZnO nanowires](image)

**Figure 2.** Comparison of XRD of nano arrays developed with ZnO (black) and Au (red).

### 3.2. Appearance distribution of ZnO nano arrays developed on Au seed layer with different concentration

The experiment is developed under Zn(NO$_3$)$_2$ · 6H$_2$O and C$_6$H$_{12}$N$_4$ (HMTA) with the same molar volume concentration for 5 hours, and the effect of concentration being 0.04 M, 0.07 M, and 0.1 M on ZnO nanowires is discussed. Figure 3a shows ZnO nanowires developed under the concentration 0.04 M, revealing that the diameter mainly grows between 0.4 μm–0.6 μm, with the average diameter about 0.45 μm and the nanowire density of 0.071 (1/μm$^2$). Figure 3b displays ZnO nanowires developed under the concentration 0.07 M; the nanowire diameter appears to be 0.6 μm–1.0 μm, with the average diameter 0.87 μm and the nanowire density 0.129 (1/μm$^2$). Figure 3c depicts ZnO nanowires developed under the concentration 0.1 M; the nanowire diameter is roughly 0.7 μm–1.0 μm, with the average diameter 0.73 μm and the nanowire density 0.216 (1/μm$^2$). The development density of ZnO nanowires increases with increasing concentration mainly because the higher concentration of Zn ions in the solution will increase the number of precursors. The mobility of precursors in the reaction solution therefore is enhanced and rapidly creates higher density and larger diameter of nanowires.

![Diameter distribution](image)

**Figure 3.** Comparison of nanowire diameters of arrays developed with (a) concentration 0.04 M, (b) concentration 0.07 M, and (c) concentration 0.1 M.
3.3 Single rod was evaluated by electron backscattering diffractometry

The electron backscattering diffractometry can apply for the microstructure observation and to identify the detailed crystallographic analysis on a rod. The side view, band contrast, phase and element map are presented in Figure 4 for the ZnO rod developed on the Au seed with the development solution of 0.1M concentration. It can be seen that every single wire is a single crystal with the same crystal orientation from the bottom to the top observed by the band contrast and phase mode. The rod consists of elements Zn and O, confirmed by the EDS element analysis attached to SEM.

![Figure 4. (a) side view and band contrast of a nanorod (b) the phase and individual element map](image)

3.4 Electricity generation characteristics of single nanowire measured with conductive atomic force microscope

![Figure 5. (a) Topography with C-AFM scanning (b) measurement of height (blue) and power generated when being knocked (red) of the correspondent red area.](image)

Figures 5a and 5b are the topography and current diagram of ZnO nanowire arrays measured with C-AFM scanning. Figure 5a shows nanowires lining up on the substrate, and the current signals of the correspondent knocked nanowires are shown in Figure 5b; the maximum could reach 800 pA. Figure 5b is the enlargement of the red selected area in Figure 5a.
4. Conclusion
The morphology of the ZnO nanowire arrays developed from the Au and ZnO seed layers of similar thickness is compared. It is found that the density of wire arrays shows significant difference and that the appearance of the array developed from ZnO seed is more interlocked and tighter compared to that from the Au seed. The preferable orientation (002) of the array developed on Au seed is perpendicular to the substrate. The diameter of the wires increases approximately with high concentration of Zn ion precursors in solution. The length of the wires increases with development time but is not correlated with the solution concentration. It is confirmed that every whole wire grown from the solution is a single crystal. The maximum current generated from a bent wire can reach 800 pA with the current geometric feature.

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