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# The epitaxial growth of ZnO nanowires for optical devices by a modified thermal evaporation method

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The epitaxial growth of ZnO nanowires over ZnO thin film deposited on silicon substrates was carried out using a modified thermal evaporation method. The precursor, which consisted of 10–30 wt.% zinc nitrate loaded over activated carbon, was prepared specifically for this study. The loading amount of zinc nitrate was varied to control the length and diameter of the ZnO nanowires. X-ray diffraction patterns confirmed that the ZnO nanowires grown on the silicon substrates were composed of typical single-crystalline ZnO. The single-crystal ZnO nanowires synthesized in this study were also studied by photoluminescence spectroscopy, and emitted intense blue UV light at around 380 nm.


*Keywords:* ZnO nanowire; Epitaxial growth; Thermal evaporation method; Activated carbon

It is known that zinc oxide is a useful semiconductor material due to its wide band gap (3.37 eV) and high excitation binding energy (60 meV) at room temperature. Zinc oxide has been studied for use in optoelectronics, electronics, catalysts and photochemistry in order to make use of its semiconducting characteristics [1–3]. Aligned ZnO nanowires have the potential to be good field electron emitters, because they have high aspect ratios, negative electron affinity and high chemical stability [4,5]. ZnO nanowires with good light-emitting properties were synthesized in this study for use in optoelectronic devices. The syntheses of the ZnO thin films and ZnO nanowires were carried out on silicon substrates. To promote the growth of ZnO nanowires with the appropriate properties for optoelectronic devices, it is generally known that a catalytic layer must first be formed on the substrates. This can be done by using metallic catalysts such as Ni and Au. Then, the single-crystalline ZnO nanowires are grown over the catalytic layer. If catalysts are used to synthesize nanowires, however, they should be removed during the fabrication of the devices. In this study, the thermal evaporation method was used to deposit a ZnO thin film acting as a seed layer for the growth of single-crystalline ZnO nanowires. The necessity of removing the catalysts was precluded by the use of this method, in which no catalysts are required in the fabrication process.

Metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE) and pulse laser deposition (PLD) require complex and expensive vacuum systems when they are used for the epitaxial growth of ZnO nanowires. On the other hand, the thermal evaporation method does not require the use of a sophisticated vacuum system, and hence has the advantage of low cost and simple operation. In the conventional thermal evaporation technique, it is difficult to control the growth direction, thickness and length of the nanowires. Therefore, in this study, a modified thermal evaporation method was developed to synthesize the desired ZnO nanowires with uniform direction and size. It is known that ZnO nanowires can be epitaxially grown on ZnO thin films. Therefore, ZnO thin films were first deposited as a buffer layer on a silicon substrate using a continuous-flow microreactor system. The use of a continuous-flow microreactor allows for the deposition of a thin film on the substrate at low temperature. ZnO nanowires were then epitaxially grown over the buffer layer without using any metallic catalysts [6]. X-ray diffraction (XRD) and scanning

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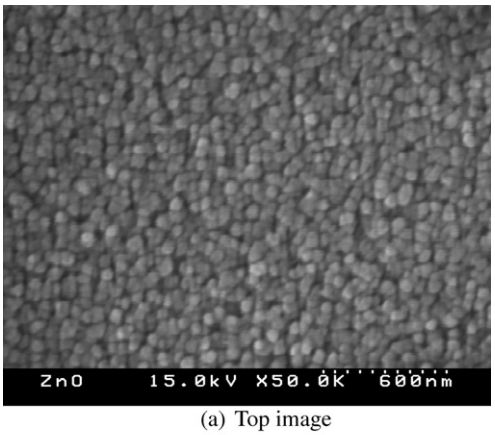
electron microscopy (SEM) were used to analyze the crystallites and the size of the ZnO nanowires, respectively. Photoluminescence (PL) spectroscopy was also used to investigate the optoelectronic properties of the synthesized ZnO nanowires.

ZnO thin films were uniformly deposited on silicon substrates using a continuous-flow microreactor system [7–9]. In the continuous-flow microreactor used in our experiments, the reactant streams A and B were initially pumped into a small tube and allowed to mix in the T-mixer. Stream A consisted of 0.005 M aqueous zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and 0.25 M aqueous ammonium acetate ($CH_3COONH_3$). Stream B consisted of a 0.005 M aqueous solution of sodium hydroxide. The period of time during which the reactants passed through the tube and the reaction temperature were 0.21 min and 90 °C, respectively. The deposited ZnO thin film was annealed at 300 °C in an air furnace. The prepared ZnO thin film deposited on the silicon substrate was used as a buffer layer for the epitaxial growth of ZnO nanowires.

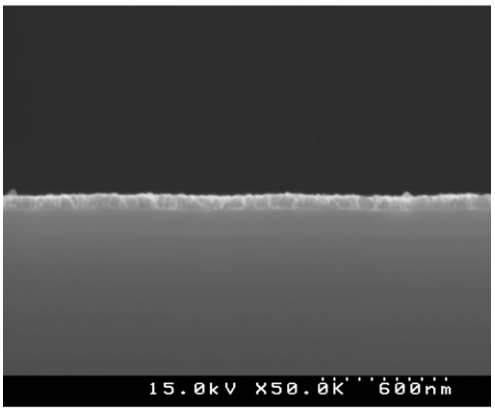
ZnO nanowires were epitaxially grown over the substrates using a thermal evaporation method. The thermal evaporation was carried out in a 50 cm long quartz reactor with a 1 in. diameter. It was placed horizontally in an electric furnace. The precursors for the growth of the ZnO nanowires were prepared by an impregnation method. That is, 10–30 wt.% zinc nitrate was loaded over activated carbon, which has a large surface area. The prepared precursors were placed in an alumina boat. The alumina boat containing the precursors and the prepared substrate were placed in the center of the reactor. Nitrogen gas containing 0.2% $O_2$ was then fed into the reactor at a flow rate of 184 ml $min^{-1}$. The temperature was increased from room temperature to 800 °C at a rate of 38.1 °C $min^{-1}$. The reactor was maintained at 800 °C for 2 h.

The phase and crystalline orientation of the ZnO nanowires were determined by XRD (Rigaku D/MAX-2500). The surface morphology of the obtained ZnO nanowires was characterized by SEM (Hitachi S-4100). The optoelectronic properties of the synthesized ZnO nanowires were also investigated by measuring their PL spectrum.

The SEM images of the ZnO thin films synthesized by the continuous-flow microreactor method are presented in Figure 1. It was confirmed that the ZnO thin film was uniformly deposited on the silicon substrate, as shown in Figure 1a. The deposited film consisted of 6–10 nm sized particles. No agglomeration of the ZnO particles was observed in the SEM images. Figure 1b presents a cross-sectional image of the ZnO thin film. It has a uniform film thickness of around 60 nm. XRD analysis was performed to investigate the crystalline structures of the as-grown ZnO structures on the silicon substrate. Figure 2 shows the XRD patterns of the ZnO thin film deposited on the substrate. All of the diffraction peaks in Figure 2 match the hexagonal ZnO structure. The (0 0 2) peak (at 34.3°) is overwhelming. ZnO nanowires are generally grown on the substrate with a non-uniform orientation. However, it is known that ZnO nanowires can be epitaxially grown on ZnO thin films [10]. The prepared ZnO thin film deposited on the silicon substrate was used as a buffer layer for the epitaxial growth of the ZnO nanowires.




(a) Top image




(b) Cross image

**Figure 1.** SEM images of ZnO thin film.

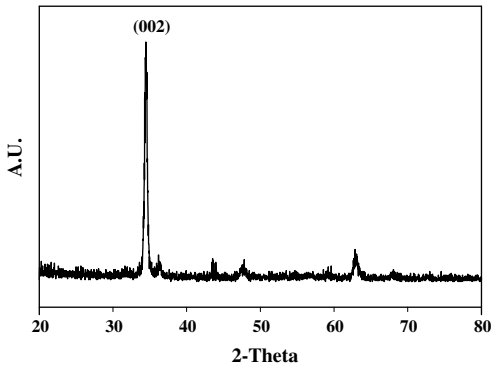



**Figure 2.** XRD patterns of ZnO thin film.

In the thermal evaporation method, the epitaxial growth of ZnO nanowires over the substrate is carried out by the evaporation of metallic zinc powder at high temperatures [11,12]. However, in this study, the growth of the ZnO nanowires was performed with the new precursor prepared by the impregnation method. Approximately 10–30 wt.% of zinc nitrate was loaded over the activated carbon. Figure 3 shows the SEM images of the ZnO nanowires synthesized by the thermal evaporation method for three different loading amounts of zinc nitrate. It was confirmed that all of the ZnO nanowires