*Journal of New Materials for Electrochemical Systems 18, 083-086 (2015)*


# Fabrication of ZnO Nanorods on Silicon Substrates by Sol-gel Hyrdothermal Methods

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Received: February 11, 2015, Accepted: April 22, 2015, Available online: June 30, 2015

***Abstract:*** *ZnO nanorods were deposited on silicon substrate using sol-gel hydrothermal methods. The seed layer was first grown by sol-gel methods and then annealed at temperatures of 300℃, 400℃, 500℃ and 600℃. Multiple material and optical analyses including field-emission scanning electron microscope, energy dispersive X-ray spectroscopy, X-ray diffraction, photoluminescence spectra, and Raman spectra were conducted to examine the growth orientation and material properties. Results indicate that the ZnO nanorods annealed at a proper temperature of 400℃ could enhance orientation and material quality.*

*Keywords: ZnO nanorods, Si substrate, sol-gel, hydrothermal, annealing*

## 1. INTRODUCTION

Over the past decade, nanostructured ZnO has attracted growing attentions because of its distinct optical, semiconducting, and piezoelectric characteristics [1-4]. Among the various ZnO nanostructures, ZnO nanorods were applied on solar cell, gas sensor, light emitting diode (LED) piezoelectric component. Until now, The fabrication of zinc oxide nanorods have been accomplished with various techniques such as chemical vapor deposition [5], sputtering [6], pulsed laser deposition [7], atomic layer deposition [8], electrochemical deposition [9], and hydrothermal method [10]. Compared with vacuum fabrication techniques, the advantages of wet deposition such as electrochemical and hydrothermal method are fast, low cost, low temperature and high efficiency [11-13]. In addition, for the wet deposition fabrication process, two-stage fabrication usually can further improve the material quality of the ZnO nanorods. For example, to fabricate ZnO nanorods with high quality, a seed layer can be first electrodeposited on a metal substrate and then ZnO nanorods can be grown by hydrothermal deposition [14]. However, for nonconductive substrates, the seed layer cannot be electrodeposited on top of the substrate. Recently, sol-gel methods, which have the benefits of fast, low cost, and power conservation, have been used to grow a precursor ZnO seed layer. According to a previous report [15], in addition to easy handling, the sol-gel method can mix various ingredients uniformly in a molecule level. Therefore, sol-gel methods can for a dense and uniformly distributed seed layer on top of the substrate. In 2008, Guo et al prepared ZnO grain seed layer by sol-gel method and the sol-gel was the mixture of zinc acetate, Ethanolamine, 2-Methoxyethanol [16]. Then, the ZnO oxide seed layer could be deposited by spin coating method on an indium tin oxide substrate. Followed by the sol-gel coating, ZnO nanorods were electrodeposited with high directivity. In this study, we grew ZnO nanorods by a two-stage sol-gel-hydrothermal technique on silicon substrates, a nonconductive substrate with potential to be integrated with Si-based semiconductors. The sol-gel and hydrothermal processes both have the advantages of simple process and power saving. In addition, rapid thermal annealing (RTA) was incorporated to the seed layer to improve the material properties of the ZnO nanorods. To investigate the material and optical properties of the ZnO nanorods, multiple material and optical analyses including field emission scanning electron microscope (FESEM), energy dispersive X-ray spectroscope (EDX), Raman, X-ray diffraction (XRD), and PL

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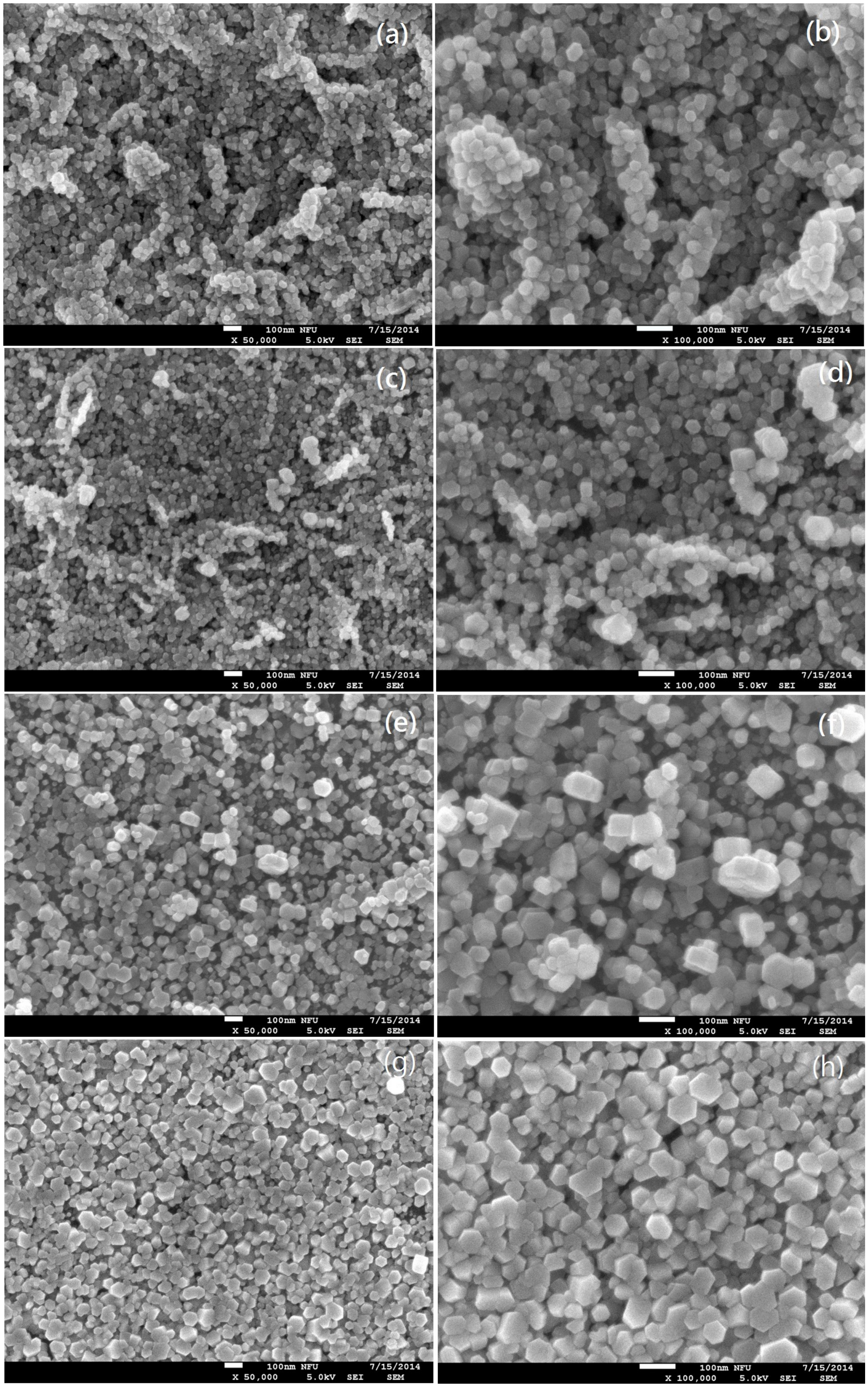


Figure 1. FESEM images of the ZnO nanorods with the seed layer annealed at (a) 300°C, (b) 300°C with a higher magnification, (c) 400°C, (d) 400°C with a higher magnification, (e) 500°C, (f) 500°C with a higher magnification, (g) 600°C, (h) 600°C with a higher magnification.

(photoluminescence) have been performed. Results indicate that ZnO nanorods with high directivity could be grown by sol-gel-hydrothermal techniques. Furthermore, the annealing of the seed layer with a proper temperature of 400ºC could further enhance the crystalline structure, improve the surface morphology crystalline structures, and eliminate the defects. The fabricated ZnO nanorods with high directivity and quality may be integrated Si-based nanodevices in the future.

## 2. EXPERIMENTAL

To fabricate ZnO nanorods on top of silicon substrates, a spin-coated seed layer by a sol-gel method was deposited on the substrate. First, the sol-gel solution was prepared by including zinc acetate, ethanol, and monoethanolamine. The 60ml ethanol was poured into the serum bottle and preheated to 60ºC. Then, zinc acetate with a concentration of 0.5 M was added into the ethanol. Functioning as a stabilizer, two drops of MEA was added from the nipple dropper into the spin coating solution. To complete the sol-gel film, the solution was stirred at 60ºC for 30 minutes. After completed the stirring and then left at room temperature for 24 hours. The sol-gel solution was spin coated on the silicon substrate. After the sol-gel film was coated on the substrate, we preheat the substrate at 130ºC for 5 minutes because preheating , could volatilize the rest of organic substances. Afterward, we repeated above spin coating 5 times. After the film coated completely, the samples were annealed with high-temperature annealing of temperatures of 300ºC, 400ºC, 500ºC and 600ºC for 1 hour, respectively. Finally, ZnO nanorods were hydrothermally grown on top of the seed layer coated substrate in the solution prepared by mixing zinc nitrate, $Zn(NO_3)_2{\cdot}6H_2O$ (0.05 M) with hexa-methylenetetramine (0.07 M). The nanorods were deposited at 80 °C for 1 hour. To characterize material properties of the nanorods, multiple material characterization instruments were performed as follows. FESEM and EDS were used to characterize the surface morphology and material composition. FESEM images and EDX spectra were measured by SM-7500F JEOL cold field emission scanning electron microscope. The crystalline structures of the films were examined by XRD Rigaku Multifex in a theta-two theta (Bragg Brentano) configuration. The XRD patterns were performed with a Cu–Kα radiation source. Raman and PL measurements were performed by Micro-Raman and Micro-PL ULVAC with light source of 532, 633, and 325 nm lasers. FESEM was used to examine the surface morphologies and EDX was used to analyze element compositions. Moreover, XRD analysis was used to examine the crystalline structures, PL was used to measure the optical properties, and Raman was used to identify the ingradients.

## 3. RESULTS AND DISCUSSION

To characterize the sol-gel-hydrothermal deposited ZnO nanorods, FESEM was used to examine the surface morphologies as shown in Fig. 1 (a)-(h). The hydrothermal grown nanorods with the seed layer annealed at 300ºC exhibited random and messy growth as shown in Fig. 1(a) and (b). As the annealing temperature increased to 400ºC, the nanorods became more orderly and better oriented as shown in Fig. 1(c) and (d). As the annealing temperature further increased to 500 and 600ºC, the nanorods became much more compact and most of the nanorods were grown vertically. The results indicate annealing temperatures higher than 300ºC could improve the orientation of the growth of the ZnO nanorods. Moreover, EDX analysis as shown in Fig. 2 was performed on the ZnO nanorods. The EDX spectra were similar for the nanorods with the seed layer annealed in various conditions indicating that the annealing might not affect the material composition of the ZnO nanorods.

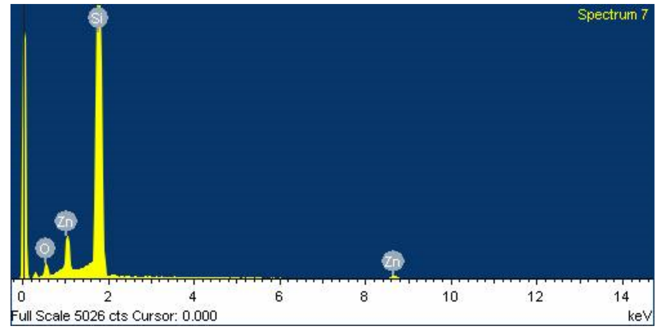


Figure 2. EDX of the ZnO nanorods.

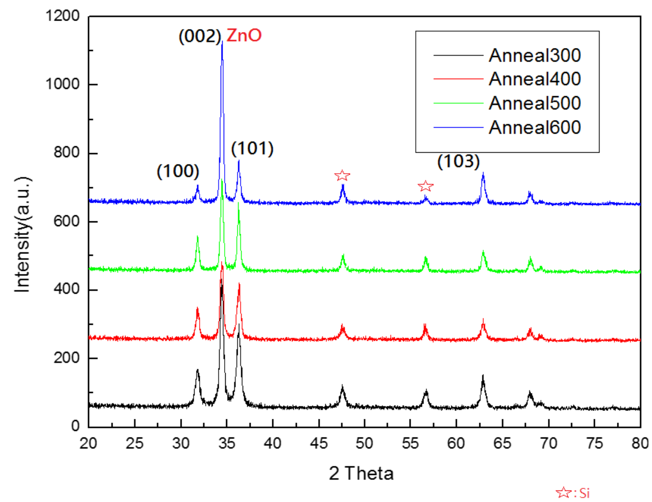


Figure 3. XRD patterns of the ZnO nanorods with the seed layer annealed in various temperatures.

To investigate the crystalline phases of the ZnO nanorods, XRD was used to study the crystalline structures of the ZnO nanorods as shown in Fig. 3. The strongest peak (002) of the ZnO nanorods is around 34°. Consistent with the FESEM images, the nanorods with the seed layer annealed above 400ºC exhibited stronger crystalline phase, indicating that annealing of the seed layer could cause the nanorods to form better crystalline structures. Furthermore, to zoom in the optical properties of the ZnO nanorods, PL spectra were taken for the nanorods with the seed layer annealed at various temperatures as shown in Fig. 4. The luminescence of the defect was around 550 nm and the luminescence of the ZnO was around 375 nm. Fig. 4 indicates that the defect luminescence could be suppressed with annealing since the nanorods with the seed layer annealed at 500 and 600ºC exhibited smaller defect luminescence intensity, indicating that the defect could be suppressed by the seed layer annealing at higher temperatures. Finally, Raman spectra were measured to evaluate the orientation degree of the ZnO nano-

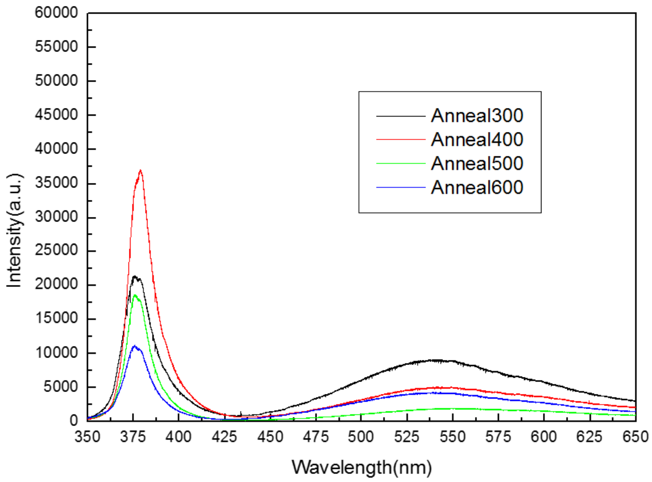


Figure 4. PL spectra of the ZnO nanorods with the seed layer annealed in various temperatures.

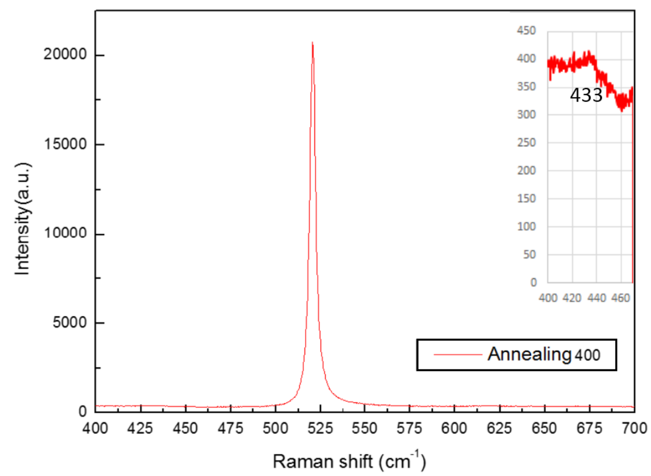


Figure 5. A Raman spectrum of the ZnO nanorods.

rods. As shown in Fig. 5, the signal of the Si substrate is around 520 $cm^{-1}$. To zoom in the ZnO signal, we enlarge the spectra around 433 $cm^{-1}$[17, 18]. A small peak of well oriented ZnO nanorods could be observed around 433 $cm^{-1}$. Based on previous reports [17, 18], the result implied that ZnO nanorods with high orientation and good material quality could be formed by sol-gel-hydrothermal methods incorporating the seed layer annealing.

## 4. CONCLUSION

In this study, ZnO nanorods were grown on top of silicon substrates by sol-gel-hydrothermal methods. The ZnO nanorods with the seed layer annealed could have high orientation and good material quality. In addition, multiple material and optical analyses were performed to examine the growth conditions. ZnO nanorods grown by sol-gel-hydrothermal methods show promises for future integration with silicon-based nanodevices.

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