

EFFECT OF HYDROTHERMAL TIME ON THE GROWTH OF ZnO NANORODS

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Abstract: In this work, ZnO nanorods (NRs) were successfully grown on printed circuit board substrates (PCBs) by utilizing a one-step, seedless, low-cost hydrothermal method. It was shown that by implementing a galvanic cell structure in an aqueous solution of 80 mM of zinc nitrate hexahydrate and hexamethylenetetramine, ZnO NRs can directly grow on the PCBs substrate without the assistance of a seed layer. The effect of hydrothermal time on the surface morphologies, and the crystallinity of the as-grown ZnO nanorods (NRs) was also investigated. The as-grown ZnO NRs also exhibited a significant enhancement in vertical growth and their crystallinity with 5 hour growth.

Keywords: ZnO nanorods; Printed circuit board (PCB); Hydrothermal method.

1. INTRODUCTION

In recent years, the development of pint-sized functional devices assembled one-dimensional nanostructures with controllably synthesized structures has attracted a lot of attention [1-5]. With unique properties such as a wide band gap of 3.37 eV and a large exciton binding energy of ~60 meV, zinc oxide (ZnO) has been recognized as a core semiconductor material utilizing in dye-sensitized solar cells, chemical and biological sensors, piezoelectric, and thermoelectric devices [6-10]. A number of surfaces such as insulating sapphire [11] and glass [12] or semiconducting Si [13] and GaN [14] were used as a base for the assembly of ZnO nanorods (NRs) in such devices. However, their applications in electronics and optoelectronics devices were hindered because of the low conductivity of these substrates. Therefore, synthesizing ZnO NRs on a metal surface is preferable in manufacturing miniaturized devices.

Among many conducting substrates, printed circuit board (PCB) containing a thin copper layer on top of insulating fiber glass is ideal for electrical and thermal conductance due to its good conductivity. However, it is difficult to grow high-quality, and vertically aligned ZnO NRs on PCBs because of the high lattice disparity between copper and zinc oxide. Furthermore, the formation of ZnO crystal seed layer normally requires a high temperature of annealing while PCBs can withstand with a relatively low temperature. As a result, the fabrication of high-quality, and vertically aligned ZnO nanostructures on PCBs is always of high demand.

In fact, several techniques have been developed to overcome this issue. For example, Chew et al. developed a method to grown high density ZnO nanowires on PCB substrates using a hydrothermal method at low temperature for memory resistor application [15, 16]. In this approach, a seed layer was deposited on the PCB substrate by using Joule heating method prior to the hydrothermal growth of ZnO nanowires. The method requires a complex, multi-step synthesis which needs an external current applied on the copper thin layer for seed layer preparation. Errico et al. and Arrabito et al., on the other hand, reported their success in synthesizing ZnO nanowires on PCB substrates using an additional adhesion layer [17], or a thin chromium film [18]. The fabricated ZnO exhibited a good vertical alignment and

adhesion. However, depositing an additional layer on top of the PCB substrates may lead to a multi-step synthesis which may introduce impurities, and exert a strong influence on the attraction between ZnO nanostructures and the substrates.

More recently, Pham et.al reported their work on seedless hydrothermal synthesizing ZnO NRs by implementing a galvanic cell structure in non-saturated equimolar aqueous solutions of zinc nitrate hexahydrate ($\text{Zn}[\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) [19]. The authors created a galvanic cell structure between a scarifying Al thin film and PCB substrate to assist the formation of a buffer layer on the copper surface. As a result, ZnO NRs can grow directly on the PCBs without the adhesion of a seed layer. However, the vertical growth of the ZnO NRs is still poor in comparison with that of seeded hydrothermal method. Another approach to grow ZnO NRs on conductive substrates is to synthesize them under saturated solution combining from $\text{Zn}[\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$ solution. It has been shown that the saturated nutrition solution helped to develop a buffer layer on the substrate, thus, the lattice mismatch between ZnO and the substrate was released. As a result, ZnO NRs can grow directly on conductive substrates without implementing a seed layer. In our previous work, for the first time, the two advanced hydrothermal methods were combined to improve the vertical growth of ZnO NRs [20, 21]. However, a detailed study on the influence of hydrothermal time on the vertical growth, and on the crystallinity of ZnO NRs is still missing.

In this paper, we investigated the influence of hydrothermal growth time on the development of ZnO NRs on PCBs by implementing a galvanic cell structure under a saturated solution of zinc nitrate hexahydrate ($\text{Zn}[\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$). The growing mechanism of the ZnO NRs was clarified when studying the surface morphologies, the vertical alignment and the crystallinity of ZnO NRs with different hydrothermal growth time.

2. EXPERIMENTAL

Sample preparation

ZnO nanorods were hydrothermally grown on PCB substrates which was assisted with a simple galvanic cell structure. The substrates were slightly rubbed with sandpaper to produce a microscale rough surface which impeded trapped bubbles leading to the non-uniform growth of ZnO NRs during hydrothermal process. Furthermore, the rough surface would enhance its contact area and adhesion of ZnO NRs. The galvanic cell structure was created by covering the copper surface of the PCBs with a thin aluminium foil exposing a small area at the center where the ZnO NRs grown (Figure 1). Both the rubbed-substrates and aluminium foils were sonically disinfected in acetone, ethanol and de-ionized water before constructing such galvanic structure.

Afterwards, the as-prepared substrates were emerged into an equivalent saturated solution of 80mM zinc nitrate hydrate ($\text{Zn}[\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$) and of 80mM hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) (Sigma Aldrich: <http://www.sigmaaldrich.com>). The substrates were placed in the solution with the temperature maintained at 90°C. To study the influence of hydrothermal time on the surface morphology,

preferable growth orientation and the crystallinity of the as-fabricated ZnO NRs, the hydrothermal growth of the ZnO on PCB substrates were carried out with a various period of time of 0.5h, 1h, 3h, 5h, 7h.

Characterization

Scanning electron microscopy (SEM) (Nova NanoSEM 450) was used to examine the sample's surface morphology. The crystallinity of the ZnO NRs was studied by X-ray diffraction (X-ray Powder Diffraction System D5000 Siemens), by Raman spectroscopy (Labram Hr800, Horiba) and by PL spectroscopy. For fluorescent measurement, a 325 nm He-Cd laser (Kimmon KOHA) was used to excite the samples and the PL emission was recorded by a spectrometer with a resolution of 0.1 nm (SP 2500i, Princeton) at room temperature.

3. RESULTS AND DISCUSSION

The hydrothermal growth process of ZnO nanocrystals was well reported elsewhere [18, 22, 23]. $\text{Zn}[\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$ provide Zn^{2+} ions while OH^- source comes from the slowly hydrolyzing process of ammonia (a product of the hydrolyte of $\text{C}_6\text{H}_{12}\text{N}_4$). The $\text{Zn}(\text{OH})_2$ compound forming from the combination between OH^- ion and Zn^{2+} ion decomposes into ZnO under given reaction conditions. In order to assist the density growth of ZnO, a galvanic structure was employed by covering the edge of the PCB substrate with an Al foil [19]. Due to the reduction potential difference between the Cu conductive layer and the Al layer, the Al acted as a sacrificing anode while the Cu functioned as a cathode. This created a bias which forced the electrons generated from the Al anode to move to the Cu cathode. This led to dissolving oxygen reaction $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$. Since the OH^- ions were increased, they could boost the nucleation of ZnO on the exposed Cu area as seen in figure 1. It has been shown that when the ZnO nuclei number was insignificant, there could be both the lateral growth and vertical growth [19]. Subsequently, the lateral growth could be suppressed due to the increasing amount of nucleation while there was a limitation in surface area.

In this work, we chose equivalent saturated concentrations of $\text{Zn}[\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$ and $\text{C}_6\text{H}_{12}\text{N}_4$ of 80 mM to assist the vertical growth of ZnO NRs. It is due to the fact that when the equimolar aqueous solution was saturated, the number of ions Zn^{2+} and OH^- was drastically increased. This resulted in the significant enhancement of ZnO nuclei which then formed a thin layer of ZnO on the surface. Such thin layer can act as a buffer layer or seed layer which can release the lattice mismatch between ZnO and the substrate. After the formation of the buffer layer, the newly arrived ions were to grow the ZnO NRs because of the lower chance of forming new nuclei than the one of reaching existing NRs. Subsequently, ZnO NRs began to grow up along c-axis preferentially on the surfaces without strain and defect. With this hydrothermal approach, vertically aligned ZnO NRs can be obtained despite the absence of additional ZnO seed layer.

The SEM images in figure 2 illustrate that the ZnO NRs underwent a gradual morphological evolution with different growth time of 0.5h, 1h, 3h, 5h and 7h. After only 0.5h of hydrothermal duration, well-aligned ZnO NRs with high density were already formed with the diameters varying from 50 to 300 nm. However, the

rods did not completely form. When the hydrothermal time was increased up to 1h, the ZnO NRs continued to grow and resulted in an increase in nanorod's diameters. For a longer hydrothermal time such as 3h and 5h, the formation of the rods was almost finished and the rods' diameter could reach up to 500 nm. This result suggests that the growth rate of ZnO NRs on PCB substrate was enhanced under the increasing of hydrothermal time which can be explained by the fact that there were higher number of nuclei on the surface of the NRs. When the hydrothermal time was long enough such as 7h, the structures were completely covered by another layer of ZnO. This is probably due the hydrothermal growth time was long enough to create another ZnO buffer layer on top of the as-grown ZnO NRs.

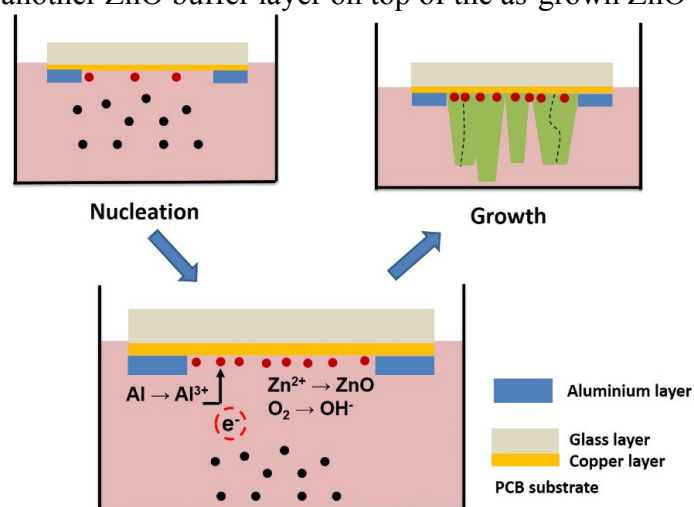


Figure 1. Schematic diagram demonstrates a seedless hydrothermal growth process of ZnO NRs on PCB substrate a) under a saturated nutrition solution, b) based on galvanic cell effect. Al is used as the sacrificing anode and PCB substrate is considered as the cathode.

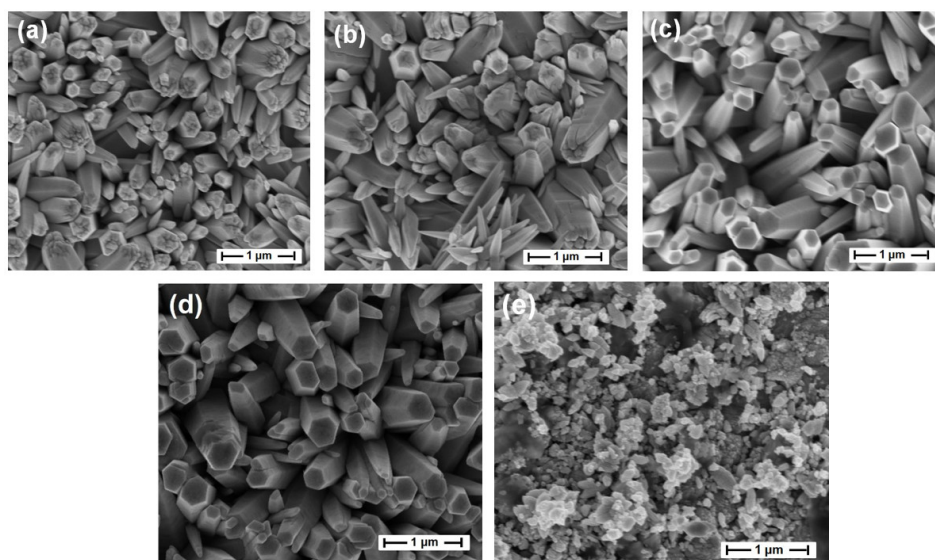


Figure 2. SEM images of the ZnO NRs with different hydrothermal time of (a) 0.5h, (b) 1h, (c) 3h, (d) 5h, (e) 7h.

Similar results were also recognized from the Xray pattern. As presented in Figure 3, the ZnO NRs preferentially grew along the (002) direction which is noticeable after only 0.5h of hydrothermal duration. When the hydrothermal time was increased further, the (002) direction became even more obvious compared to the (100) and (010) direction. The highest intensity ratios between the (002) peak and the two neighbouring peaks were obtained with 5h of hydrothermal growth sample, denoting the best vertical orientation. The vertical orientation got worse in the case of 7h hydrothermal time which can be attributed to the generation of a buffer layer.

The effect of the hydrothermal time on the crystallinity of the ZnO NRs was investigated by Raman and PL spectroscopy. As seen in Figure 4, the two typical peaks of ZnO Raman spectra at 98 cm^{-1} and 437 cm^{-1} were observed [24-26]. Furthermore, they became sharper with higher intensity with respect to the increase of hydrothermal time from 0.5h to 5h. This indicates the best crystallinity was obtained with samples of 5h hydrothermal time.

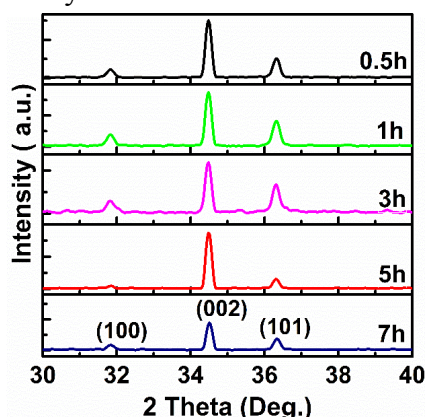


Figure 3. X-ray patterns of the as-grown ZnO NRs with different hydrothermal time.

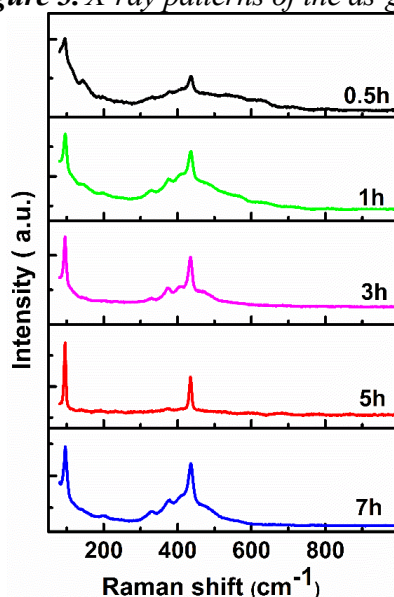


Figure 4. Raman scattering spectra of the as-grown ZnO NRs with different hydrothermal time.

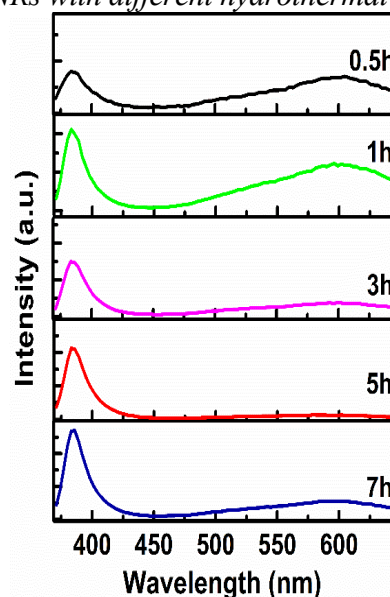


Figure 5. Photoluminescent spectra of the as-grown ZnO NRs with different hydrothermal time.

The room temperature PL spectra of the ZnO NRs with different hydrothermal growth times were presented in Figure 5. Generally speaking, a PL spectrum of ZnO normally contains a narrow UV emission peak at 384 nm, and a broad green emission band at 610 nm [25, 27]. Good crystallinity of ZnO can be valued by the high intensity ratio of the two bands. As seen from the figure, the ratio is significantly improved with respect to the increase of the hydrothermal duration from 0.5 to 5h, and represents a slight decrease when the growth time reaches 7h. The highest intensity ratio was obtained with the sample of 5h hydrothermal time, denoting the best crystallinity of the as-grown ZnO NRs. The high density, high surface to volume ratio and the high crystallinity of the 5h growth sample demonstrate promising applications of the as-grown ZnO NRs in electronics and photonics devices.

4. CONCLUSION

In this work, ZnO NRs were successfully grown on PCB substrate by a simple, one-step, low-cost, seedless hydrothermal method. It was demonstrated that hydrothermal growth time created a strong impact on the vertical alignment and the crystallinity of the as-grown ZnO NRs on PCB substrate. The SEM, XRay, Raman and PL spectra have confirmed the improvements in both vertical alignment and crystallinity during duration growth time of ZnO NRs from 0.5 to 7 h. The best results were obtained with 5h hydrothermal time. The high density, high crystallinity of the as-grown ZnO NRs are important factors for their future applications in electronics and photonics devices.

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TÓM TẮT

NGHIÊN CỨU ẢNH HƯỞNG CỦA THỜI GIAN THỦY NHIỆT TỚI SỰ HÌNH THÀNH THANH NANO ZnO

Trong nghiên cứu này, các thanh nano ZnO đã được mọc trên đế điện cực in (PCB) sử dụng phương pháp thủy nhiệt đơn giản, giá thành rẻ thông qua chỉ một bước tổng hợp. Bằng cách ứng dụng hiệu ứng pin galvanic trong dung dịch thủy nhiệt gồm 80 mM $\text{Zn}(\text{NO}_3)_2$ và 80 mM $\text{C}_6\text{H}_{12}\text{N}_4$, thanh nano ZnO có thể mọc trên đế PCB mà không cần có sự hỗ trợ của lớp mầm ZnO. Ảnh hưởng của thời gian thủy nhiệt lên hình thái bề mặt và độ kết tinh, cũng như cường độ huỳnh quang của thanh nano ZnO đã được nghiên cứu. Các kết quả cho thấy rằng thanh nano ZnO có thể mọc dày đặc trên đế PCB với độ định hướng tốt nhất, và độ kết tinh cao nhất sau khi được thủy nhiệt trong thời gian là 5 giờ.

Từ khóa: Thanh nano ZnO; Đế mạch in PCB; Phương pháp thủy nhiệt.

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