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Epitaxial Growth of ZnO Nanowires Over the ZnO Thin Films Deposited on the Si and Sapphire Substrates

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Epitaxial growth of ZnO nanowires was carried out using a modified thermal evaporation method with inexpensive experimental setup. ZnO nanowires were synthesized using ZnO thin films. The ZnO thin films were deposited as a buffer layer on silicon and sapphire using an impinging flow reactor (IFR). The IFR system is a modified version of a chemical bath deposition (CBD). Films can be created at low temperature, without any metallic catalysts. The properties of Zinc Oxide films are dependant upon the type of substrate used. The same deposition process with a different substrates yields two films with different properties. The most critical effect on growth of ZnO nanowires were dependent the properties of the buffer layer deposited on the substrate. It was not the type of substrate used. A cost-efficient method for epitaxial growth of single crystal ZnO nanowires is proposed in this work.

Keywords: Single Crystal ZnO Nanowire, Epitaxial Growth, ZnO Thin Layer, Modified Thermal Evaporation Method, Impinging Flow Method.

RESEARCH ARTICLE

1. INTRODUCTION

It is known that zinc oxide is a useful material for semiconductor use due to its wide band gap (3.37 eV) and its high excitation binding energy (60 meV) at room temperature. Zinc oxide has been studied for use in catalysts, electronics, optoelectronics and photochemistry in order to utilize its semiconductor characteristics.[1–5] Aligned ZnO nanowires could be used as good field electron emitters because they have high aspect ratios, negative electron affinity and high chemical stability.[6] ZnO nanowires were synthesized in this study for use in optoelectronic devices, because of their good lasting effect. The syntheses of ZnO thin films and ZnO nanowires were carried out on silicone or sapphire substrates. To grow the ZnO nanowires with the appropriate properties for optoelectronic devices, it is known that a catalytic layer must first be formed on the substrates. This can be done using metallic catalysts such as Ni and Au. Then a single crystalline ZnO nanowires were grown over the catalytic layer.[6] If catalysts are used to synthesize nanowires, the catalysts should be removed during fabrication of devices. It is very difficult to remove the catalysts from the substrates. New methods such as Metal Organic Chemical Vapor Deposition (MOCVD), Molecular Beam Epitaxy (MBE) and Thermal Evaporation, which do not require catalysts for the process, were introduced to resolve this problem.[2] However, MOCVD and MBE require a complex and expensive systems for the epitaxial growth of ZnO nanowires. The thermal evaporation method has an advantage due to its low cost and simple operation. It does not require sophisticated vacuum systems or expensive equipment. The thermal evaporation technique makes it difficult to control the growth direction, thickness, and length of the nanowires.[7] It was known that ZnO nanowires were epitaxially well grown on ZnO thin films.[8] A modified thermal evaporation method was created to achieve the desired ZnO nanowires with uniform direction and size. In this study, ZnO thin films were first deposited as a buffer layer on both silicone and sapphire substrates using an impinging flow reactor (IFR) system. This is a modified version of a chemical bath deposition (CBD). The IFR allows for deposition at low temperatures. Then ZnO nanowires were epitaxially grown over the buffer layer without using any metallic catalysts.[9–10] Depending upon the type of substrate used in the study, X-ray diffraction (XRD) and scanning electron microscope (SEM) were used to analyze the crystallites and size of ZnO nanowires, respectively. Photoluminescence spectrum was also used to investigate the optoelectronic properties of the synthesized ZnO nanowires.

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2. EXPERIMENTAL DETAILS

2.1. Preparation of ZnO Thin Films on Silicon and Sapphire Substrates

In this study, silicon (100) plane, the *c*-plane of sapphire, and the *r*-plane of sapphire were used as substrates. ZnO thin films were deposited on those substrates using an impinging flow reactor system.[11] For this IFR system reactant streams A and B were initially pumped into a small tube. They were then mixed using a T-mixer. Stream A consisted of 0.005 M aqueous zinc acetate dihydrate and 0.25 M aqueous ammonium acetate. Stream B consisted of 0.005 M aqueous solution of sodium hydroxide. The resulting mixture passed through a 10 foot long tube, which was immersed in a hot water bath. The bath was maintained between 70–90 °C. The solution was impinged on the substrate. The substrate was taped to a stainless steel metallic hot plate and heated at 100 °C. The period of time and a flow rate of solution for impinging were 3 minutes and 14.85 ml/min. Once the process was completed, the substrate was removed from the plate, and washed with DI water. It was then dried with a stream of nitrogen gas.

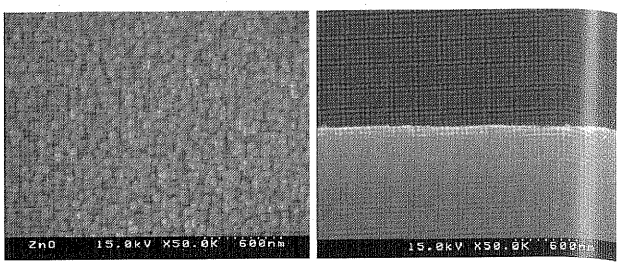
2.2. Epitaxial Growth ZnO Nanowires

ZnO nanwires were epitaxially grown over the substrates using a thermal evaporation method. The wires were grown at temperature higher than 800 °C. The thermal evaporation was carried out in a 50 cm long quartz reactor with a 2 inch diameter. It was placed horizontally in an electric furnace. The alumina boat containing the precursors and the prepared substrate were placed in the center of the reactor. A mixture of 99.8% N_2 and 0.2% O_2 were charged into the reactor to oxidize Zn. Precursors for the growth of ZnO nanowires were prepared by loading 20 wt% zinc acetate over activated carbon, which has a large surface area. About 0.2 grams of the prepared precursors were placed in the alumina boat. Then the nitrogen gas containing 0.2% O_2 was fed into the reactor with a flow rate of 184 ml/min. Temperature was increased from room temperature to 800 °C at a rate of 38.7 °C/min. The reactor was maintained at 800 °C for 2 hours. Then it was cooled by natural air convection. Silicon and sapphire substrates, with ZnO thin films deposited by IFR, were used in this study. SEM, XRD, and Photoluminescence (PL) were used to analyze the characteristics of the synthesized ZnO nanowires.

3. RESULTS AND DISCUSSION

3.1. ZnO Thin Film on the Various Substrates

Various substrates were used to grow ZnO nanowires. The properties of ZnO thin films deposited as a buffer layer

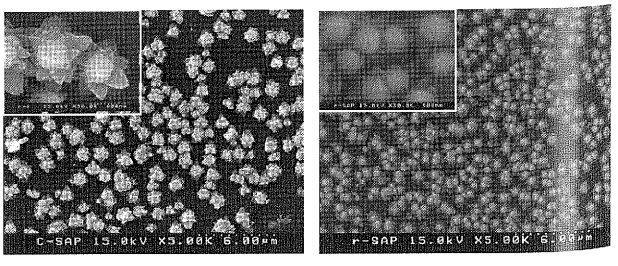


(a) (b)

Fig. 1. SEM images of ZnO thin film synthesized by the impinging flow method on the silicon substrate.

on the substrate were dependent upon the type of substrate used for the study. ZnO thin films were synthesized using an IFR system over the substrate. The IFR method has significant advantages for the deposition of thin films over large areas. The SEM images of the ZnO thin film synthesized by the IFR method are presented in Figures 1 and 2. As shown in Figure 1(a), it was confirmed that the ZnO thin films were uniformly deposited on the silicon substrates. Agglomeration of ZnO particles were not observed in the SEM images. Figure 1(b) presents a cross-sectional image of a ZnO thin film. It has a uniform film thickness around 60 nm. It is believed that the IFR system overcame the obstacles involved with CBD processes by providing strict control of particle size and its distribution by adjusting the product solution impinged on the substrate. ZnO thin films were synthesized using a IFR system over sapphire substrates. However, instead of the ZnO thin films, flower-like ZnO structures were formed over the substrate as shown in Figure 2. Different substrates yielded films with different ZnO film morphologies despite using the same deposition process. In addition, the synthesized flower-like ZnO structures deposited over the sapphire substrates showed different morphologies because the direction of the crystal growth was affected.

XRD analysis was employed to investigate the crystalline structures of the as-grown ZnO structures on each substrate. Figure 3 shows the XRD patterns of the ZnO structures grown the silicone and sapphire substrates. All diffraction peaks in Figure 3(a) match the hexagonal ZnO structures. The (002) peak (at 34.3°) is overwhelming.



(a) (b)

Fig. 2. SEM images of ZnO thin film on the sapphire substrates: (a) the *c*-plane oriented sapphire substrate and (b) the *r*-plane oriented sapphire substrate.

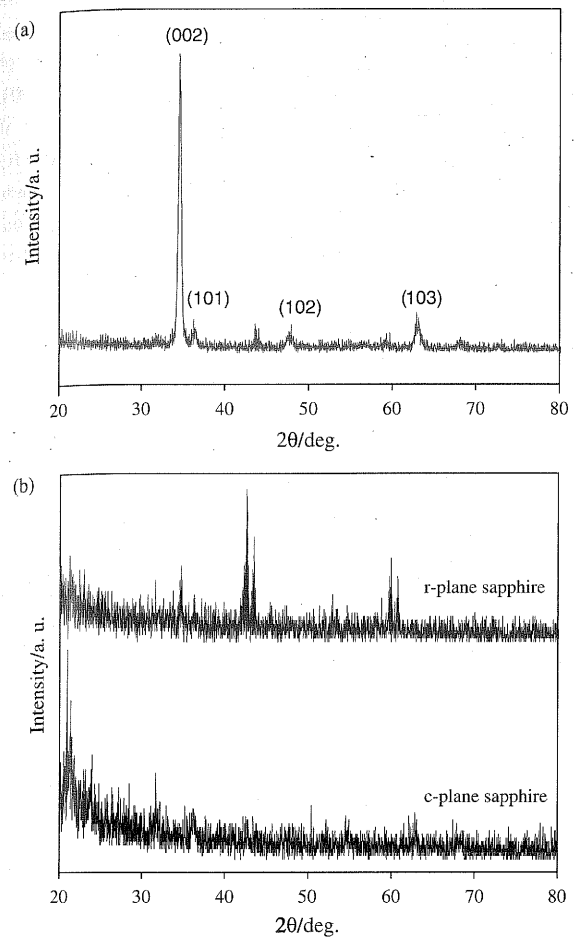


Fig. 3. XRD patterns of the ZnO thin films on the substrates (a) the silicone substrate and (b) the sapphire substrates (c- and r-plane).

Fujimura et al.[12] suggests that the surface energy density of the (002) orientation is the lowest in the ZnO crystal. It was confirmed that the ZnO crystal grown on silicon substrate forms the film. However, the ZnO structure grown on the sapphire substrate is amorphous, as shown in Figure 3(b). From the SEM and XRD analysis, it was confirmed that the deposited ZnO showed different morphologies and crystallinities based on the type of substrate used for the growth of ZnO films.

3.2. Epitaxial Growth of ZnO Nanowires on Silicon Substrates

As described above, ZnO nanowires were epitaxially synthesized using a modified thermal evaporation method over ZnO thin film. Thin films were deposited as a buffer layer on silicon substrate by the IFR system. A precursor of Zn was used for the growth of ZnO nanowires. It was prepared by loading 20 wt% zinc acetate over activated carbon, which has a large surface area. The deposition of ZnO over the substrate is performed by evaporation of metallic zinc powder.[13–15] In this study a precursor was prepared for the growth of ZnO nanowires. Figure 4(a) shows SEM

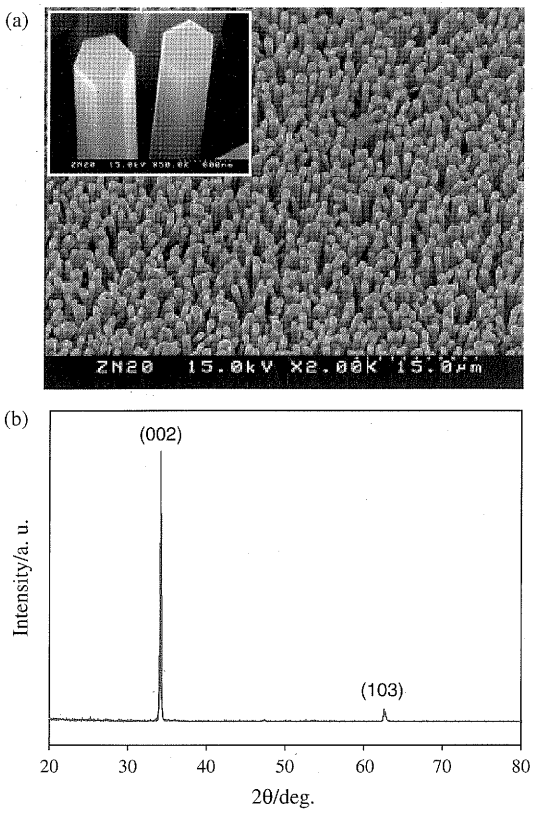
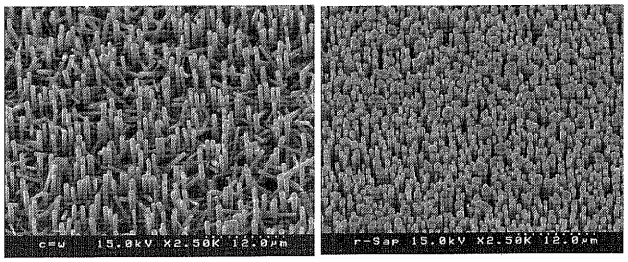


Fig. 4. (a) SEM images and (b) XRD pattern of ZnO nanowires synthesized by the thermal evaporation method over ZnO thin film on the silicone substrate.

images of ZnO nanowires synthesized using the thermal evaporation method over ZnO thin film on silicon substrate. The synthesized ZnO nanowire arrays on silicone substrates are of a single crystalline structure with uniform length (900–1500 nm) and diameter (~600 nm). They are evenly distributed over the substrate with one direction. The experiment confirmed that most of the nanowires were hexagonal wurtzite ZnO. This can be seen by crystal in the XRD measurement as shown in Figure 4(b). Peaks at $2\theta \approx 34.4°$ and 62.8° are attributed to (002) and (103) ZnO orientations, respectively. All diffraction peaks in Figure 4(b) match hexagonal ZnO crystal. It was determined by the properties of ZnO thin film deposited on silicon substrate. Since ZnO thin films on the substrate were grown in the direction of the c-axis in the structure of single crystalline, ZnO nanowires were grown over the thin film perpendicular to the substrate. It is well known that ZnO nanowires are grown in the direction of the c-axis.[16–18]

3.3. Epitaxial Growth of ZnO Nanowires on Sapphire Substrates

ZnO thin films were synthesized over sapphire substrates. These thin films were used to grow the GaN thin films for LED. Then ZnO nanowires were grown over the produced ZnO thin films. Two different sapphire substrates oriented in c-plane and r-plane, were used in this



(a) (b)

Fig. 5. SEM images of ZnO nanowires over ZnO thin film on the sapphire substrates; (a) on the *c*-plane sapphire and (b) on the *r*-plane sapphire.

study. ZnO nanowires were synthesized over the sapphire substrate using the same conditions used on silicon substrates. However, the morphologies of the ZnO nanowires grown on the *c*-plane of sapphire substrates were different from the morphologies of silicone substrates. Figure 5 presents SEM images of ZnO nanowires grown on ZnO thin films on *c*-plane and *r*-plane sapphire substrates. ZnO nanowires formed on the *c*-plane of sapphire had anisotropic dimensional growth as shown in Figure 5(a). While ZnO nanowires synthesized on the *r*-plane of sapphire had unidirectional growth, shown in Figure 5(b), ZnO nanowire growth depended on the substrate having specific crystal direction.

The phase and crystalline orientation of the ZnO nanowires synthesized on two different sapphire substrates were determined by XRD and presented in Figure 6. In the XRD patterns, ZnO nanowires grown on the *c*-plane of sapphire substrate, show a (002) peak at $2\theta \approx 34.4°$ and a (101) peak at $2\theta \approx 36.2°$. These peaks showed the strongest intensity as presented in Figure 6(a). A ZnO unit cell positioned at the starting point of the nanowire growth has a tetrapod structure. The center of the structure exists in a state of the mixed crystallines. These crystallines encountered various directional orientations. The tetrapod structure is considered a typical polycrystalline structure.

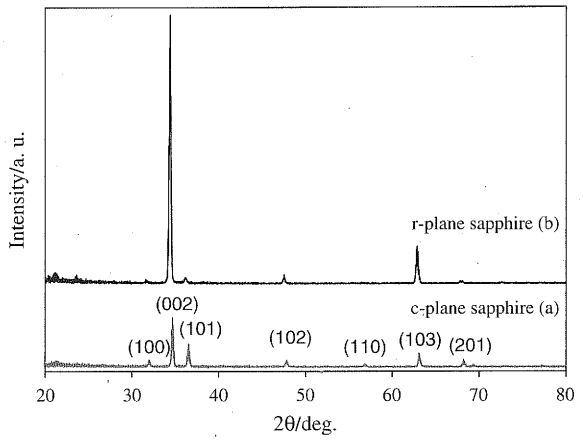


Fig. 6. XRD patterns of ZnO nanowires over ZnO thin film on the sapphire substrates; (a) on the *c*-plane sapphire and (b) on the *r*-plane sapphire.

Polycrystalline ZnO shows particular XRD peak patterns depending upon the crystalline structure. The intensity of XRD peaks for polycrystalline ZnO are at 31.7° (100), 34.4° (002), and 36.2° (101). These are in the ratio of 57:44:100. It was indicated that the polycrystalline ZnO would form in the center of the tetrapod structure starting a nucleation.[19] All XRD spectra confirmed that the polycrystalline ZnO and the single crystal ZnO coexist in the ZnO nanowires were grown on the *c*-plane of sapphire substrate. It is consistent with the morphology of ZnO nanowires formed on *c*-planes of sapphire to have multi-directional growth seen in Figure 5(a). The formation of the polycrystalline ZnO structures, which serve as the nucleation centers on the substrate cause the coexistence of two different crystal structures. Figure 6(b) shows the XRD peaks of ZnO nanowires formed on the *r*-plane of a sapphire substrate. The (002) peak at $2\theta \approx 34.4°$ confirms the single crystal ZnO. This is consistent with SEM images of ZnO nanowires formed on the *r*-plane of sapphire shown in Figure 5(b). Based on experimental results, it is believed that the most critical effect to the growth of ZnO nanowires are the properties of the buffer layer deposited on the substrate, instead of, the type of substrate. Since ZnO buffer layer was grown in the shape of a flower bud in the direction perpendicular to the substrate as presented in Figure 2(b), ZnO nanowires was also grown in the direction perpendicular to the substrate regardless of the characteristics of the substrate. Therefore, the tetrapod structure formed on the *c*-plane of sapphire was not observed in ZnO nanowires formed on the *r*-plane of sapphire. The only peak corresponding to the (002) orientation was observed in XRD analysis. This peak was formed because the single crystalline was grown perpendicular to the substrates.

3.4. Photoluminescence of ZnO Nanowires on Various Substrates

PL spectra of the ZnO nanowires epitaxially grown on silicon and sapphire are shown in Figure 7. Single crystal ZnO nanowires emit intensive blue UV light around 380 nm. In PL spectrum, ZnO nanowires on silicon substrates have a sharp PL peak. This is clearly observed around 380 nm as shown in Figure 7(a). The very broad PL peak around at 550 nm might be caused by crystal defects. PL spectrum of the ZnO nanowires varied with the substrate used for the study. ZnO nanowires grown on silicon substrate emitted intensive blue UV light, but the ZnO nanowires formed on sapphire substrates emitted a very weak blue light. This is presented in Figure 7(b and c). Instead, a strong broad peak in yellow band of light was observed for the PL spectra of the ZnO nanowires. It seemed that the crystalline orientation of the sapphire substrate did not have considerable influence on the growth of ZnO nanowires. The formed ZnO nanowires were

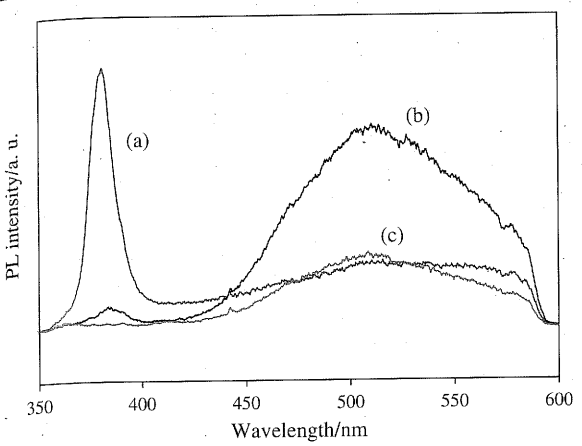


Fig. 7. Photoluminescence spectra of ZnO nanowires over the ZnO thin film on three different substrates; (a) on the silicone substrate, (b) on the *r*-plane sapphire, (c) on the *c*-plane sapphire.

expected to have single crystal structure and uniform crystalline orientation. They were also expected to emit an intensive blue UV light. However, PL spectrum of the ZnO nanowires depended upon the substrate used for this study. From previous SEM images and XRD measurements, the PL peak at 380 nm was intensely emitted when the direction of crystal growth was perpendicular to the substrate and ZnO nanowires were single crystalline in structure. ZnO nanowires synthesized on silicon substrates and on the *r*-plane of sapphire substrates were single crystals and were grown perpendicularly to the substrate. Nevertheless, no blue UV light emission in the PL spectrum for ZnO nanowires on the *r*-plane of sapphire substrates were created by the ZnO structures deposited over the substrates. In this study, ZnO synthesized on sapphire substrates by the IFR system had flower-like structures instead of thin films. Flower-like ZnO structures were not aligned well in one direction, and the polycrystalline ZnO structures were formed in the center of the flower-like structures. Because of these two facts it was believed that the PL spectrum of ZnO nanowires grown on the *r*-plane of sapphire substrates was different from the ZnO nanowires grown over ZnO thin film on silicon substrates.

4. CONCLUSION

A modified thermal evaporation method with an inexpensive experimental setup was employed for the epitaxial growth of ZnO nanowires. The well-aligned ZnO nanowires were synthesized over ZnO thin films. These were deposited as a buffer layer on silicon and sapphire by the IFR system. The influence of substrate used in the formation of the ZnO nanowires was investigated. Different substrates used to grow ZnO nanowires deposited ZnO thin films showed different properties. This was true even when the same deposition process was used. It was confirmed that the most critical effect for the growth of ZnO nanowires was the properties of the buffer layer deposited on the substrate instead of the type of the substrate used. The growth direction of ZnO nanowires was determined by the growth direction of ZnO crystalline formed over the buffer layer instead of the growth direction of the substrate. ZnO nanowires emitting intensive blue UV light for the application to the optoelectronic devices were synthesized. Single crystalline ZnO thin films should be formed on the substrate. The more cost-efficient method for the growth of single crystal ZnO nanowires on silicon substrates was proposed in this work.

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