Vertically Well-Aligned ZnO Nanowires on $c\text{-}Al_2O_3$ and GaN Substrates by Au Catalyst

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ABSTRACT—In this letter, we report that vertically well-aligned ZnO nanowires were grown on GaN epilayers and c-plane sapphire via a vapor-liquid-solid process by introducing a 3 nm Au thin film as a catalyst. In our experiments, epitaxially grown ZnO nanowires on Au-coated GaN were vertically well-aligned, while nanowires normally tilted from the surface when grown on Au-coated c-Al_2O_3 substrates. However, pre-growth annealing of the Au thin layer on c-Al_2O_3 resulted in the growth of well-aligned nanowires in a normal surface direction. High-resolution transmission electron microscopy measurements showed that the grown nanowires have a hexagonal c-axis orientation with a single-crystalline structure.

Keywords—ZnO, nanowire, c-Al_2O_3, GaN, CVD, HRTEM.

I. Introduction

Recently, quasi-one-dimensional (1D) ZnO nanostructures such as nanowires [1], [2], nanorods [3], and nanobelts [4] have attracted great interest due to their unique electrical and photonic properties for possible applications in optoelectronics, chemical sensors, and field-effect transistors. Realization of vertically well-aligned 1D ZnO nanostructures has been considered for application to nanoscale light-emitting diodes (LEDs), nanosensors, and field emitters [3], [5], [6]. Fabrication of 1D ZnO nanostructures has been demonstrated using various methods including thermal evaporation, thermal chemical vapor deposition (CVD), metalorganic chemical vapor deposition (MOCVD), and the sol-gel process [1]-[3], [7]. The VLS process is commonly introduced to achieve vertically well-aligned ZnO nanowires on lattice-matched substrates such as GaN, highly oriented pyrolytic graphite (HOPG), or a-plane Al_2O_3 [8], [9]. GaN is a very promising substrate for the epitaxial growth of ZnO nanowires due to the similar lattice constant of GaN and ZnO. Recently, the catalyst-free MOCVD-synthesis of ZnO nanowire arrays on a p-type GaN layer was reported by W.I. Park and others [3]. In that study, the electroluminescence from the n-ZnO nanowire/p-GaN thin film heterojunctions was investigated, showing the possibility of realizing n-ZnO/p-GaN nanowire heterojunction LEDs and laser diodes with high efficiency. However, GaN, a-plane Al_2O_3, and HOPG substrates are quite expensive. This indicates that the epitaxial growth of vertically well-aligned ZnO nanowires on c-plane Al_2O_3 (0001) substrates is one of the most important issues in the ZnO research community for realizing nanoscale ZnO-based light-emitting devices, even though there are several difficulties such as the significant lattice mismatch between ZnO and c-Al_2O_3. In this regard, we report the epitaxial growth of ZnO nanowires on both GaN epilayers and c-plane Al_2O_3 substrates using the VLS mechanism in a CVD process.

II. Experiments

Undoped GaN epilayers with 4 μm thickness were grown by MOCVD on c-Al_2O_3 substrates. Prior to the nanowire growth in a tube furnace, the Au thin layer (3 nm) deposited on GaN epilayers and c-Al_2O_3 substrates was used as a catalyst for the synthesis of highly aligned ZnO nanowires. This was achieved by evaporating a mixture of ZnO (99.999% purity) and graphite (99.99% purity) powder (1:1) in an Ar-ambient atmosphere. The Au-coated

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substrates were placed 1 cm downstream from the center of the tube. On the equilibrium of the Ar gas flow at 700 sccm, the tube was heated and kept at 970-990°C for 90 min. The as-grown samples were characterized by field-emission scanning electron microscopy (FE-SEM), and X-ray diffraction (XRD) using a standard diffractometer with Co Kα radiation in the θ-2θ configuration and *high-resolution transmission electron microscopy* (HRTEM) measurements.

III. Results and Discussion

Figure 1 shows FE-SEM images of vertically well-aligned ZnO nanowire arrays grown on GaN epilayers at 970 and 980°C. The nanowires grown for 90 minutes in this study are around 50-100 nm in diameter and around 1-3 μm long. As shown in Fig. 1, all the nanowires grown on GaN epilayers are uniformly oriented with almost no nanowires tilted from the surface (not common on GaN epilayers), although there is a slight difference in nanowire morphology between the two samples. The orientation of the nanowire arrays to the GaN epilayer was further investigated by XRD measurements. ZnO nanowires were found to have an epitaxial relation between the GaN epilayers and the ZnO nanowires. The c-axis oriented GaN and ZnO have almost overlapping XRD profiles due to their similar lattice constants. As shown in Fig. 2, there are no additional peaks other than (0002) and (0004) peaks, indicating good alignment of the ZnO nanowires along the c-axis direction on GaN.

A low-magnification TEM image of the single nanowire shown in Fig. 3(a) clearly shows that the ZnO nanowires with a diameter of around 80 nm on GaN originated from the VLS process. The HRTEM image shown in Fig. 3(b) clearly shows a well-resolved lattice with an interplanar spacing of about 0.52 nm and that the nanowires grew along the [0001] direction. The inset of Fig. 3(b) is the selected area electron diffraction (SAED) pattern, which is more evidence of the c-axis oriented growth of ZnO nanowires on GaN epilayers. Our ZnO nanowires on GaN epilayers are of a single-crystalline hexagonal structure and c-axis orientation.

Growth of ZnO nanowires on c-Al_2O_3 substrates coated with the as-deposited Au film (3 nm) results in the formation of nanowires (with interdigitated morphology) normally tilted from the surface on c-Al_2O_3 substrates as shown in Fig. 4(a). However, pre-growth annealing of the Au thin layer on c-Al_2O_3 resulted in the growth of well-aligned nanowires with diameters of around 120 nm in the appropriate surface direction as shown in Fig. 4(b). This indicates that thermal treatment at 920°C in an Ar ambient prior to the main ZnO growth at 990°C for 90 minutes promotes the vertical growth of ZnO nanowires on c-Al_2O_3 substrates. The XRD pattern of vertically well-aligned ZnO nanowires on the c-Al_2O_3 substrate is shown in Fig. 4(c). The diffraction pattern indicates that the ZnO nanowire sample grown on the thermally-treated Au-coated c-Al_2O_3 substrate exhibits a hexagonal ZnO crystal structure showing strong (0002) and (0004) peaks. This indicates that most of our ZnO nanowires are vertically well-aligned on the c-Al_2O_3 substrates and are of a strongly preferred orientation along the c-axis.

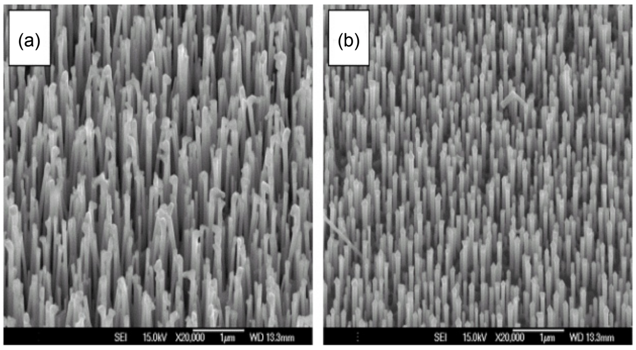

Fig. 1. FE-SEM images of vertically well-aligned ZnO nanowires grown on GaN epilayers at 970°C (a) and 980°C (b) for 90 min.

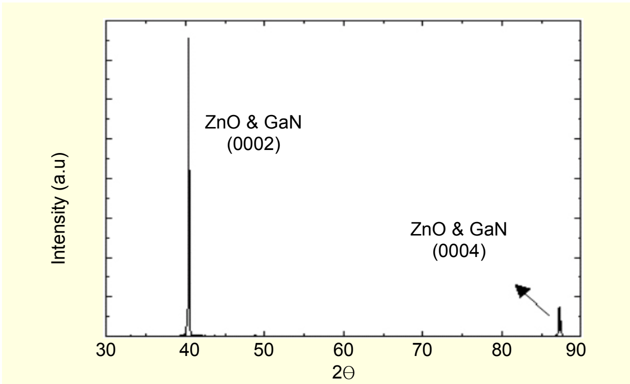

Fig. 2. XRD pattern of ZnO nanowires grown at 980°C on the GaN epilayer.

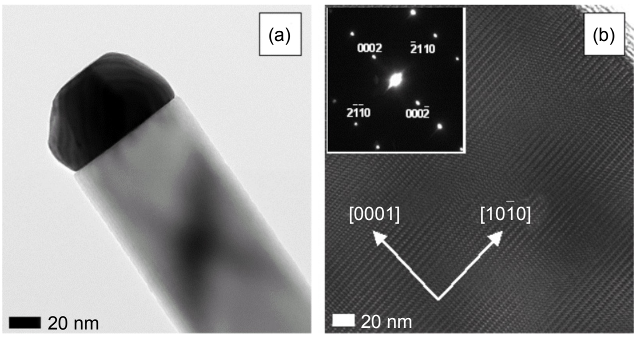

Fig. 3. (a) Low-magnification TEM image of a single nanowire grown on the GaN epilayer, clearly showing that nanowire formation originates from the VLS process. (b) HRTEM image lattice image as well as a SAED pattern (inset) at the edge of the single nanowire, confirming that the nanowire is of the single-crystalline hexagonal structure and c-axis orientation.

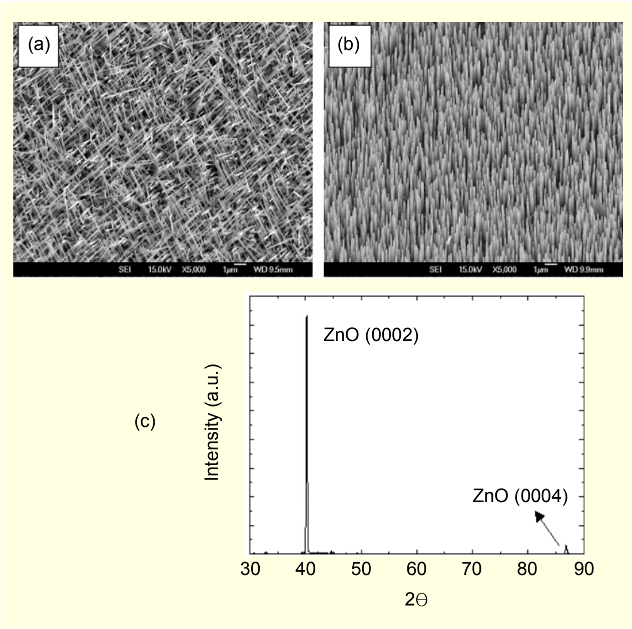

Fig. 4. (a) Tilted ZnO nanowires on the c-Al_2O_3 substrate coated with the as-deposited Au catalytic layer. (b) Vertically well-aligned ZnO nanowires on the annealed Au layer/ c-Al_2O_3 substrate. (c) XRD pattern of the ZnO nanowire sample shown in Fig. 4(b).

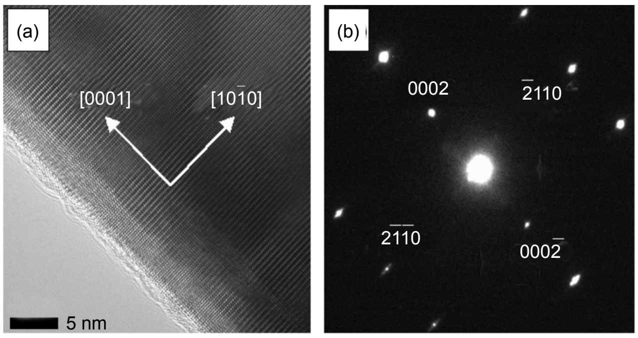

Fig. 5. (a) HRTEM image and (b) SAED pattern of a single nanowire shown in Fig. 4(b).

Recently, Nikoobakht and others [10] reported that the growth direction of ZnO nanowires on c-Al_2O_3 substrates can be controlled by pre-growth annealing of the Au catalyst layer in accordance with our results. They suggested that the absence of annealing of the c-Al_2O_3 substrates causes an Al-terminated c-Al_2O_3 surface, resulting in the formation of nanowires tilted from the surface which is normal on c-Al_2O_3 substrates due to the effective growth of nanowires on facets [(11$\bar{2}$0) plane]. On the other hand, pre-growth annealing of the Au catalyst layer causes an O-terminated c-Al_2O_3 surface having an [0001] orientation. Therefore, we conclude that the thermal treatment of the Au catalyst layer promoted the vertical growth of the ZnO nanowires on c-Al_2O_3 substrates. In accordance with the above XRD result, the HRTEM image and SAED pattern shown in Fig. 5 clearly show that the single nanowire grown on the pre-growth annealed c-Al_2O_3 substrate is single-crystalline wurtzite structured and c-axis elongated.

IV. Conclusion

Vertically well-aligned ZnO nanowires were fabricated on GaN epilayers and c-Al_2O_3 substrates using the VLS process. The substrate is important parameter in the morphology and growth direction of ZnO nanowires. The ZnO nanowires on GaN epilayers were uniformly formed. TEM measurements showed that our nanowires on are of a single-crystalline hexagonal structure and c-axis orientation. In addition, we could also realize vertically well-aligned ZnO nanowires on c-Al_2O_3 substrates by introducing pre-growth annealing of the Au-catalytic layer. Our investigations in this study would be very helpful for realizing well-aligned ZnO nanowires on a large scale.

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