

Fabrication of ZnO hybrid structures and light emitting diode applications

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ABSTRACT

Vertically-aligned ZnO nanorod arrays with a diameter of 40 - 150 nm were fabricated on Al₂O₃ substrates with and without GaN interlayers, and consequently covered with a ZnO film *in-situ* by a catalyst-free metal-organic chemical vapor deposition method. X-ray diffraction and transmission electron microscopy measurements demonstrated that the ZnO film/nanorods hybrid structures had a well-ordered wurtzite structure with no lattice mismatch between the film and nanorods, and that the film was homoepitaxially grown horizontally as well as vertically on the pre-grown nanorods. From *n*-ZnO film/nanorods/*p*-GaN hetero-junctions, we observed an asymmetry rectifying behavior.

Keywords: ZnO, nanorod, MOCVD, film, LED

1 INTRODUCTION

ZnO is attractive for practical applications to light emitting diodes (LEDs) and optoelectronic devices at room temperature (RT) because of its wide band gap of 3.36 eV and high exciton binding energy of 60 meV at room temperature (RT) [1]. Furthermore, the energy band gap can be changed by substituting a small amount of Mg or Cd ions [2-5]. GaN has similar physical properties to ZnO, including a same wurtzite (WZ) structure, similar lattice constants, and a similar band gap energy of 3.39 eV. In addition, GaN is widely used for practical applications to ultraviolet (UV) LEDs and laser diodes. There have been numerous attempts to develop ZnO/GaN heterostructures for LED applications [6-9] However, it has been recognized that the efficiency of a *p-n* heterojunction is lower than that of a homojunction. Park *et al.* reported a possible efficiency enhancement of the ZnO/GaN heterojunction using ZnO nanostructures [6].

ZnO nanowires, carbon nanotubes, ZnS nanoparticles, CdSe nanoparticles, Si nanowires, and GaN nanowires were intensively investigated for their practical applications. However, for industrial applications of nanostructures, several tens to thousands of the nanobuilding blocks are needed for a single device because practical devices require stability, reproducibility and sufficiently long life. Bundles

of ZnO nanowires with a hierarchical pattern were fabricated by a Langmuir-Blodgett technique for transistor applications [10] while vertically aligned ZnO nanorods fabricated with a metal-organic chemical-vapor deposition (MOCVD) procedure were filled with polymer [6], and covered with an amorphous ZnO layer for LED applications [9]. Park *et al.* demonstrated that a two-dimensional (2D) crystalline film could be epitaxially grown on the pre-grown on one-dimensional (1D) nanorods [11]. In this article, we discuss the 2D growth on 1D nanorods with a catalyst-free MOCVD method and the structural properties of the ZnO film/nanorods hybrid structures. The ZnO film/nanorods heterostructures can be widely used for nanodevice applications, including nano LEDs, gas sensors, bio-sensors, computer memory devices, easily flipping chips from substrates.

2 EXPERIMENTS

Vertically aligned ZnO nanorod arrays were synthesized by a catalyst-free MOCVD procedure on Al₂O₃ (0001) substrates with and without *n*-type and *p*-type GaN interlayers [12]. DEZn (diethylzinc, Zn(C₂H₅)₂) and high purity oxygen (99.9999%) were used as zinc and oxygen precursors, respectively. During the ZnO nanorod growth, the substrate temperature and chamber pressure were maintained at 350 - 500 °C and 0.2 - 0.4 Torr, respectively. The DEZn precursor was directly flowed into the MOCVD reaction chamber with Ar carrier gas. The inflow rates of the precursor and carrier gas were monitored by an electrical pressure controller and a mass flow controller, respectively. The inflow ratio of the oxygen to DEZn precursor was maintained at about 300 : 1. A ZnO film was subsequently deposited *in-situ* on the pre-grown ZnO nanorods at the chamber pressure of 2-3Torr. The dimensional growth from 1D to 2D was simply controlled by only the growth chamber pressure. The field-emission scanning electron microscopy (FE-SEM) images demonstrated that the ZnO crystals were grown horizontally and only within a certain region of the top part of the nanorods, leading to a very uniform film thickness, as shown in Fig. 1 (b) and (c). The GaN interlayers were deposited on the Al₂O₃ (0001) substrates by a high-temperature, low-pressure MOCVD method. Trimethylgallium (TMGa), trimethylindium (TMIn),

trimethylaluminum (TMAI), bis-cyclopentadienyl magnesium (Cp_2Mg) and ammonia (NH_3) were used as precursors at the substrate temperature of 900 – 950 °C.

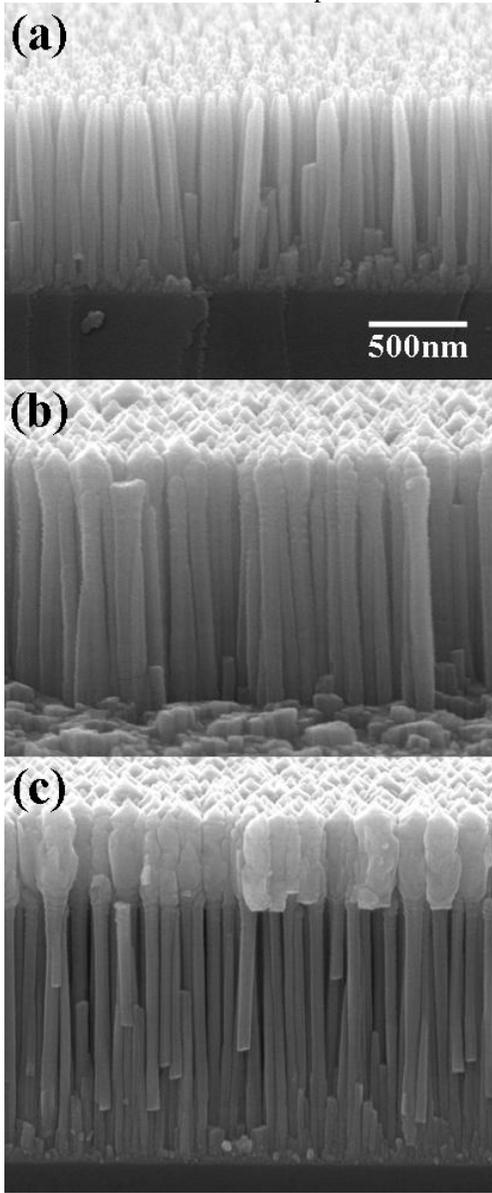


Figure 1. FE-SEM images of (a) as-grown ZnO nanorods on Al_2O_3 , (b) the initial growth at a high chamber pressure, (c) a homo-epitaxially grown ZnO film on ZnO nanorods. The nanorod length was about $1 \mu\text{m}$ and the film thickness was about $0.25 \mu\text{m}$.

3 RESULTS AND DISCUSSION

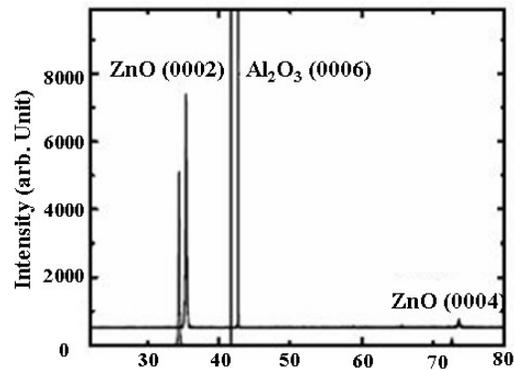


Figure 2. XRD from (top) ZnO nanorods and (bottom) ZnO film/nanorods equate with the specimens in Figs. 1(a) and (c), respectively, as a function of 2θ .

The FE-SEM images in Figs. 1 demonstrate ZnO nanorods and the growth steps of a ZnO film on the pre-grown ZnO nanorods. Vertically-aligned ZnO nanorods have been synthesized on various substrates without any catalyst, including Al_2O_3 , n-GaN, p-GaN and Si. A ZnO film can be synthesized on the vertically-aligned ZnO nanorods *in-situ* and *ex-situ* by using MOCVD regardless of the species of the substrates. Figure 1 (c) shows a ZnO film with thickness of $\sim 0.25 \mu\text{m}$ uniformly covering pre-grown ZnO nanorods on a GaN interlayer. At a low chamber pressure, the ZnO formed into vertically aligned nanorods. The diameter of the nanorods was dependent on the substrate temperature. At a high chamber pressure, the ZnO crystals were vertically as well as horizontally growing on the pre-grown ZnO nanorods. The ratio of vertical to horizontal growth was determined by the spatial gradients of the temperature and pressure at the growing surface. A low temperature or a high pressure stabilized a small spatial gradient, so that the ZnO was growing at the top and lateral surface of the ZnO nanorods. It has been recognized that the terminating atoms at the lateral surface of the ZnO nanorods were oxygen. The terminating oxygen and surface passivation during increasing the chamber pressure may prevent additional ZnO growth in the lower region of the nanorods at a high pressure growth. As the substrate temperature is lower, one can also expect the horizontal and vertical growth of ZnO in the MOCVD method. The ZnO might form a film on the pre-grown ZnO nanorods. However, it was reported that the ZnO film solidated at a low temperature was amorphous or polycrystalline. This can be understood in term of surface energy. Zinc and oxygen reactants at the growing surface may not have sufficient kinetic energy to form a crystalline structure at a low temperature. The ZnO growth in vertical and horizontal directions at a high pressure was more clearly seen by atomic force microscopy (AFM).

To characterize the crystal structure and structural residual strain of the ZnO hybrid structures such as ZnO film/nanorods, X-ray diffraction (XRD) measurements were performed as shown in Fig. 2. The XRD measurements revealed that there was neither an extra

phase nor a diffraction peak separation. This strongly suggests that the ZnO film/nanorods is a single crystal with a well ordered wurzite structure, and that the ZnO film was epitaxially grown on the pre-grown ZnO nanorods along the c-axis of the sapphire substrate. The lattice constant c of 5.2055 Å was estimated from the ZnO (0002) and Al₂O₃ (0006) diffraction peaks. This result agrees well with those of the ZnO bulk and nanorods [13]. The full width at half maximum of the (0002) diffraction peak from the ZnO film/nanorods was 0.140°, compared to 0.204° from the non-film ZnO nanorods, implying that the structural residual strain in the ZnO film on the ZnO nanorods is smaller than that of the non-film ZnO nanorods.

The local structural properties of a selected area of the nanorods with an initial film growth at their tops were characterized with field-emission transmission electron microscopy (FE-TEM) measurements. Figure 3 demonstrates the FE-TEM images of the nanorods with an initial film growth at their tops. The high-resolution FE-TEM image (b) from the top part of the nanorods demonstrates the defect-free atomic layers. These XRD and FE-TEM results demonstrated that the crystallization of the ZnO film grown on ZnO nanorods was greatly enhanced compared to that reported in a previous study [9], as the ZnO film was solidated on the pre-grown ZnO nanorods by controlling the growth chamber pressure rather than by adjusting the other growth parameters, such as substrate temperature.

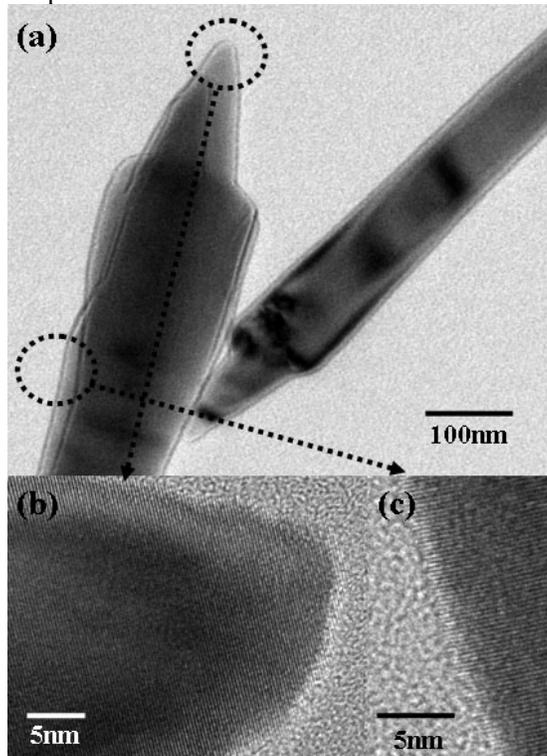


Figure 3. (a) FE-TEM images from ZnO nanorod array with a bud shape at the top of the nanorods. (b) and (c) High resolution FE-TEM images from the top part and the near lateral surface of the nanorod indicated by the dotted

circles.

For LED applications, the ZnO film/nanorods were synthesized on a p -type GaN film with the thickness of 0.1 μm, as shown in the inset of Fig. 4. The p -type GaN interlayer was deposited on an Al₂O₃ (0001) substrate using MOCVD while bis-cyclopentadienyl magnesium (Cp₂Mg) was used as the precursor for the p -doping. The average charge carrier density was about $1 \times 10^{18} \text{ cm}^{-3}$. Subsequently, the ZnO nanorods and film were epitaxially grown on the p -GaN interlayer with catalyst-free MOCVD. Ohmic contacts were simply fabricated by evaporating Ti/Au and Pt/Au bilayers on the n -ZnO film/nanorods and the p -GaN layer, respectively, without any extra process. Rapid thermal annealing enhanced the Ohmic contacts. RT I - V measurements from the n -ZnO nanorods/ p -GaN heterostructures are shown in Fig. 4. The asymmetry rectifying behavior of the I - V characteristic curves demonstrated the building of the p - n junction across the heterostructure. At the forward bias, no current delay implied good Ohmic contacts at both interfaces of metal/ n -ZnO and metal/ p -GaN with a negligible Schottky barrier. However, a small breakdown voltage suggested the presence of a leakage current at the junction.

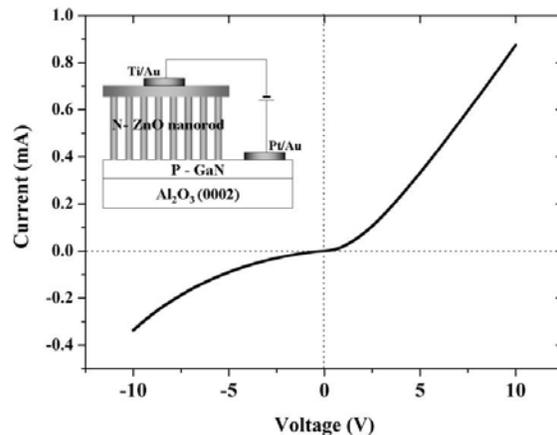


Figure 4. I - V characteristic curves of an n -ZnO nanorod/ p -GaN hybrid structure at RT. The inset shows a schematic illustration of I - V measurements on the n -ZnO nanorods/ p -GaN heterostructure.

4 CONCLUSIONS

A uniform crystalline ZnO film was grown on ZnO nanorods with a catalyst-free MOCVD procedure. Vertically well aligned 1D-ZnO nanorods were fabricated, and subsequently, a 2D ZnO film was deposited on the pre-grown ZnO nanorods in-situ at high chamber pressure. By controlling the chamber pressure, we greatly improved the quality and uniformity of ZnO film grown on pre-grown ZnO nanorods. The 2D film growth at only the top region of the pre-grown 1D nanorods was attributed to the advantage of the MOCVD technique because a relatively high growth pressure of 2 - 3 Torr for the film growth might assist in passivating the lateral surface of the

nanorods, and because the flow of the precursors could restrict the crystal growth to the top region of the nanorods. We suggested an idea of 2D film growth on 1D nanorods in the MOCVD method with spatial gradients of temperature and pressure. However, the growth mechanism of the 2D film on the 1D nanorods is still unclear, and remains to be elucidated in further study. These film/nanorods structures cannot be made by a top-down technique, such as lithography. Metal layers for Ohmic contact or films can be easily deposited on the film/nanorods structures without any extra process. In addition, these nanostructures still preserve the merits of nanostructures, including a large volume-surface ratio and more energy density states near the band edge. This alternative growth technique of 1D or 2D can be widely used to fabricate nanostructures for practical nanodevice applications.

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