

## Epitaxial growth of ZnO film on patterned n-GaN layer by hydrothermal method

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### Abstract

The hetero-epitaxial growth of ZnO film on patterned n-GaN/sapphire(0001) substrate by hydrothermal growth technique is demonstrated for the first time. The prepared ZnO films are with single crystalline and wurtzite structure as revealed by XRD  $\phi$ -scan and HRTEM analysis. With experimental evidences obtained from different stages of the HTG process, possible growth mechanism for the epitaxial growth ZnO film on patterned n-GaN layer is proposed and discussed.

### 1. Introduction

ZnO nanostructures have attracted considerable attention recent years because of their potential applications in light-emission nano-devices, solid-state sensors and field emitters [1]. Numerous techniques have been employed for the synthesis of ZnO nanostructures. Among them, the hydrothermal growth (HTG) method is attractive because it is a low-temperature and low-cost process that is especially suitable for large-area production. Though high quality ZnO films are urgently needed for device applications, the synthesis of ZnO using HTG, using ZnO- or GaN-based seed layer usually yields wire/rod/sheet type nanostructures or film-like layers comprising of dense ZnO rods [2].

In essential, there are three key types of growth mechanisms including Frank-van der Merwe Mode (layer-by-layer), Stanski-Krastanov Mode (layer to island), and Volmer-Weber Mode (island) [3] that might involve with the growth of epitaxial layers, depending on the degree of lattice mismatch between the substrate and the grown material. Since ZnO and GaN have the same wurtzite structure, and lattice mismatch between them along the c-axis is 0.4% which is much less than that of 1.88% along a-axis, hetero-epitaxy of ZnO on GaN can be expected. However, due to the surface energy of ZnO  $\{10\bar{1}0\}$  planes is much less than that of  $\{11\bar{2}0\}$  or  $\{0001\}$  planes [4] and having 1.88% lattice mismatch with a-axis of GaN, the synthesis of ZnO on c-plane of GaN substrate would follow the "layer to island" growth mode and usually result in wire-type nanostructures [5, 6]. Nevertheless, it is reported that, for the homo- or hetero-epitaxy of ZnO [7-9], the ZnO  $\{0002\}$  planes (with a d space of 0.26 nm) could always coherent with those crystal planes that have a similar d space, under the circumstances, it might lead to an epitaxial growth on  $\{10\bar{1}0\}$  planes without the occurrence of any boundary on c-plane [8].

In this work, to our knowledge, hetero-epitaxial HTG growth of crystalline ZnO film on patterned n-GaN layer is reported for the first time. The surface n-GaN layer is intentionally etched to form circular holes to provide nucleation sites for the hetero-epitaxial HTG of ZnO nanorods along their side walls. These highly coherent rods then served as templates for the consequent lateral growth of ZnO films with aligned orientation. Effect of the etching pattern on the epitaxial growth of continuous ZnO films is examined. Material qualities of the prepared ZnO films are investigated using HRTEM, SEM, and XRD  $\phi$ -scan analysis. Experimental evidences obtained from different stages of the HTG process are reported. Possible growth mechanism for the epitaxial growth ZnO film on patterned n-GaN layer is proposed and discussed.

### 2. Experiment

Fig. 1 illustrates the key processes for the hetero-epitaxial growth of ZnO films on patterned n-GaN surface using HTG method. A honeycomb pattern array shown in upright illustrates the pattern suitable for the film growth, which is with a hole diameter (D) and distance (L) of 3 and 6  $\mu\text{m}$ ,

respectively.

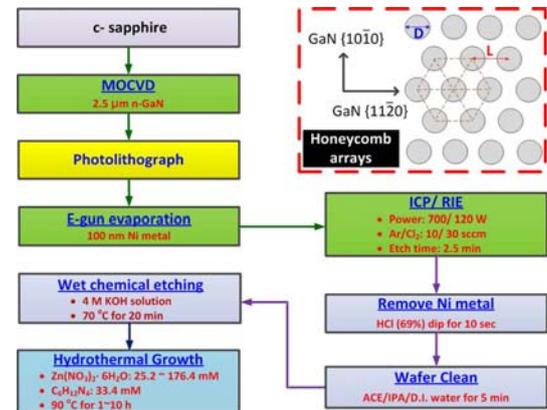


Fig. 1 Key processes for the hetero-epitaxial growth of ZnO films on patterned n-GaN layer using a two-step HTG method.

The n-GaN layer grown by MOCVD system on c-plane sapphire substrate is with a thickness of 2.5  $\mu\text{m}$  and a carrier concentration of around  $1 \times 10^{18} \text{ cm}^{-3}$ . The pattern on the GaN layer was formed via photolithography with an e-beam sputtering deposited 100-nm-thick Ni mask and inductive-coupled plasma (ICP) etching. Typical depth of the etched hole is around 1.3  $\mu\text{m}$ . Note that the size, distance, and depth of the etched hole play the crucial role in the ZnO growth.

The GaN epitaxial wafer was subjected to a cleaning process using acetone, isopropanol, and D.I. water and a chemical etching using 70°C/4M KOH for 20 min to remove native  $\text{Ga}_2\text{O}_3$  layer before HTG process. Chemical solutions with 33.4 mM hexamethylenetetramine and different mole concentrations of zinc nitrate: 25.2 mM (6 g  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} / 800 \text{ ml}$ , named as 1X solution), 50.4 mM (3X), 126 mM (5X), and 176.4 mM (7X), were used for the HTG growth of ZnO films. The growth temperature was set constant at 90°C. To clarify possible growth mechanism of the hetero-epitaxy of HTG ZnO films, samples are prepared for different HTG times. In addition, to facilitate a complete layer of HTG ZnO film, a 2<sup>nd</sup> HTG growth in a new 5X solution was conducted. For material characterization, FESEM was used to examine the grown ZnO samples. Quality and structure of the prepared ZnO films XRD were characterized by XRD and HRTEM.

### 3. Results and Discussion

Fig. 2(a)~(c) show the SEM images of samples after HTG growth for 1, 2, and 8 h in HTG solution with 25.2 mM  $\text{Zn}^{+2}$  mole concentration (1X) in the 1<sup>st</sup> growth stage. Coherence of nuclei to form ZnO NWs on the side wall of the etched hole for the 1 h sample was observed (Fig. 2(a)), which should be attributed to lattice mismatch along c-axis is much lower than that along a-axis. For the 2 h sample, advanced coherence of neighboring NWs via c-axis leads to the formation of a hollow ZnO crystals with hexagonal-shape rim covering the etched hole region of the n-GaN layer. Further increasing the HTG time, with nucleation sites providing from the sidewalls and a much less surface energy along the ZnO  $\{10\bar{1}0\}$  planes as compared with that of the  $\{11\bar{2}0\}$  or  $\{0001\}$  planes, ZnO layer extend laterally (i.e., grow inwards and outwards simultaneously), which results in the shrinkage of the hollow in the center portion of the ZnO crystals (Fig. 2(c)). Fig. 2(d) shows the sample grown with a higher 3X solution for 6 h, complete hexagonal-shape ZnO crystals with no hollow are achieved. Note that all the grown hexagonal ZnO crystals align along the corresponding edge, i.e., all ZnO crystals are with exactly the same

ZnO{0002} crystal plane. It suggests that a perfect coherence of crystal planes should occur during the HTG process. As shown in Figs. 2(e) and 2(f) for 10 h HTG time, the size of grown hexagonal-shape ZnO crystals increases with increasing HTG time and mole concentration of zinc nitrate. For the 5X-10 h case (Fig. 2(f)), intimate connection of neighboring ZnO crystals is seen.

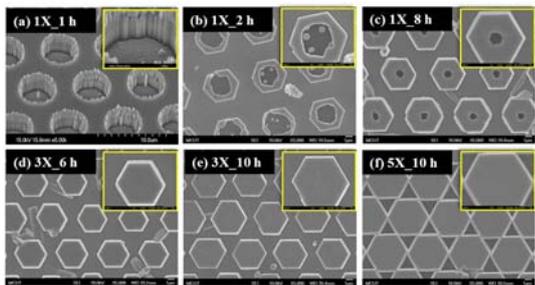


Fig. 2 SEM images showing ZnO crystallites grown on n-GaN with honeycomb pattern hole array in HTG solution with zinc nitrate of 25.2 mM solution at 90°C for (a) 1h (b) 2 h (c) 8 h, and 75.6 mM (3X) for (d) 6 h (e) 10 h, and 126 mM (5X) for (f) 10 h. All images have the same scale bar.

In our experience, further lengthening HTG time, e.g., 5X-12h or 7X-10h, the surface of the grown ZnO layer might be dissolved due to the exhaust of Zn source in the HTG solution precursor in the HTG. To continue the supply of Zn to grow a continuous ZnO film, a new HTG solution with 126 mM zinc nitrate (5X) was used for the 2<sup>nd</sup> stage HTG growth. Fig. 3 shows the top and side view of the sample prepared after the 2<sup>nd</sup> stage HTG for 10 h. a 5.25- $\mu\text{m}$ -thick ZnO layer with a complete plane and an excellent ZnO{0002} in-plane coherence grown along the direction of c-plane was formed.

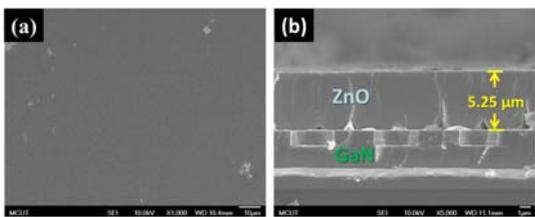


Fig. 3 SEM images of the ZnO film obtained from the proposed two-step HTG process on patterned n-GaN layer using a solution with 126 mM zinc nitrate (5X) at 90°C for 10 h. (a) top view and (b) side view.

Fig. 4(a) shows the FESEM image of the FIB-cut ZnO film after the 2<sup>nd</sup> stage growth. Though voids appear at the bottom of the grown ZnO layer around the center of the etched hole and the half-way of two neighboring holes, quite good quality of the continuous ZnO film grown above the GaN surface is evident from the figure. Based on HRTEM image shown in Fig. 4(b), it is seen that the crystal orientation of the grown ZnO layer is in perfect alignment with that of the GaN, i.e., (0002)<sub>GaN</sub>//(0002)<sub>ZnO</sub> and (1010)<sub>GaN</sub>//(1010)<sub>ZnO</sub>. The SAD pattern shown in Fig. 4(c) reveals that only the  $\bar{3}030$  diffraction points can be discriminated because of the existence of a relative large lattice mismatch along the a-axis direction, while along the c-axis direction, diffraction points from ZnO and GaN even for 0006 coincide with each other.

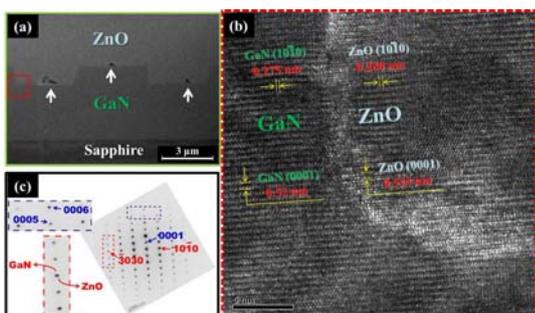


Fig. 4 (a) FESEM image of the cross-sectional view of the grown ZnO film. (b) HRTEM images, and (c) SAD pattern of the same sample.

Fig. 5(a) shows the XRD ( $\theta$ -2 $\theta$  scan) pattern of the grown ZnO films. It reveals that the (0002) diffraction peak of ZnO thin film is merged with the respective diffraction peaks of n-GaN thin film due to a close lattice matching (ZnO(0002)//GaN(0002)//Al<sub>2</sub>O<sub>3</sub>(0006)). The XRD pattern reflects that the HTG ZnO film is with wurtzite structure and orientation along the c-axis. Fig. 5(b) shows the  $\phi$ -scan patterns of the GaN and ZnO films. It indicates clearly the six-fold symmetry of the wurtzite structure of ZnO and n-GaN. The similar angular positions of the respective peaks of ZnO and n-GaN suggests that the HTG ZnO film and the n-GaN layer have the epitaxial relationship of (0002)[11 $\bar{2}0$ ]<sub>ZnO</sub>//(0002)[11 $\bar{2}0$ ]<sub>GaN</sub>. The full-width at half maximum (FWHM) of ZnO and GaN measured from the theta rocking curve are 0.134 and 0.135°, respectively, it confirms that the ZnO films prepared from the two-step HTG growth on patterned GaN layer is single crystalline with a high crystal quality.

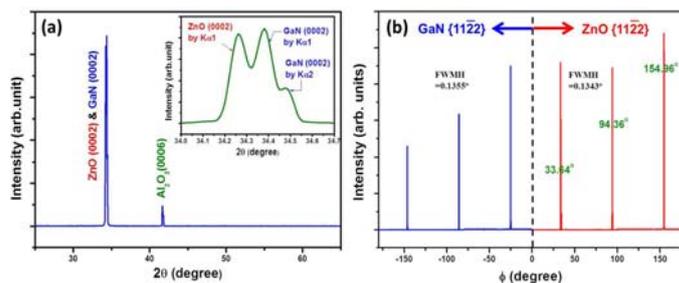


Fig. 5 Results of XRD analysis. (a)  $\theta$ -2 $\theta$  scan pattern. Inset shows the K $\alpha$ 1 and K $\alpha$ 2 diffraction pattern with 34-34.7°. (b) {1122} plane  $\phi$ -scan, indicating both GaN and ZnO layer are single crystalline.

#### 4. Conclusions

A successful hetero-epitaxial growth of ZnO single crystalline ZnO films by a two-step HTG process on patterned GaN layer has been demonstrated for the first time. Since lattice mismatch along the c-axis is much less than that of the a-axis, side walls of the patterned holes offer nucleation sites for the formation of initial nuclei with coherent (0002) plane to form hexagonal ZnO nanorods in the initial stage, after that, a consequent lateral growth of ZnO films with sufficient Zn supply from the 2<sup>nd</sup> HTG growth process leads to lateral epitaxial growth of ZnO film with high crystalline quality. Possible growth mechanism for the hetero-epitaxy of HTG ZnO film on patterned GaN layer has been clarified according experimental evidences. It is expected that the scheme for the growth of crystalline ZnO film proposed in the present study could promote potential device applications in the near future.

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