

## Research Article

# Growth and Characterization of High-Quality GaN Nanowires on PZnO and PGaN by Thermal Evaporation

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In the current research, an easy and inexpensive method is used to synthesize highly crystalline gallium nitride (GaN) nanowires (NWs) on two different substrates [i.e., porous zinc oxide (PZnO) and porous gallium nitride (PGaN)] on Si (111) wafer by thermal evaporation without any catalyst. Microstructural studies by scanning electron microscopy and transmission electron microscope measurements reveal the role of the substrates in the nucleation and alignment of the GaN NWs. Further structural and optical characterizations were performed using high-resolution X-ray diffraction, energy-dispersive X-ray spectroscopy, and photoluminescence spectroscopy. Results indicate that the NWs have a single-crystal hexagonal GaN structure and growth direction in the (0001) plane. The quality and density of GaN NWs grown on different substrates are highly dependent on the lattice mismatch between the NWs and their substrates. Results indicate that NWs grown on PGaN have better quality and higher density compared to NWs on PZnO.

## 1. Introduction

Group III nitrides have emerged in the past decade as materials of choice for blue and UV optoelectronic devices, as well as high-power, high-frequency electronics. Knowledge of the surface electronic structure and its dependence on the surface polarity and growth conditions is of fundamental importance [1]. One-dimensional growth of wide bandgap semiconductor such as GaN (3.4 eV) nanostructures holds considerable technological applications for nanodevices, such as LEDs and solar cells [2–4].

Several methods to grow one-dimensional GaN nanostructures have been developed to account for the catalyst-induced gallium nitride (GaN) nanowires (NWs). Nevertheless, recent papers have found that NW contamination caused by the catalyst considerably limits the structural and optical quality of NWs. However, only a small number of basic works have been devoted to the investigation of the physical mechanisms that account for the self-induced growth of GaN NWs [5].

Recently vapour phase and chemical methods dominate NW growth to produce semiconductor devices [6–9]. These

methods are steady-state techniques and provide a better control of NWs' growth, in contrast to solution methods [10]. But these methods are expensive and also are not easy to do. So, the most important focus on current photovoltaic cell research is finding new methods to improve device efficiency, safety, and cost.

Herein we report an easy, cheap, and successful method, based on thermal evaporation method in an atmosphere of argon (Ar) gas (no ammonia gas was used), to produce highly crystalline GaN NWs on PZnO and PGaN substrates. The influences of the substrates, PZnO and PGaN, on the composition and morphology of these NWs have been investigated.

## 2. Experiment

Alumina boats were used to hold the commercial GaN powder and the substrates. Thermal evaporation was used to produce GaN NWs under the flow of argon (Ar) gas, without any catalyst to assist in the preparation. The NWs were synthesized inside a tube furnace for 2 h. In each experiment,

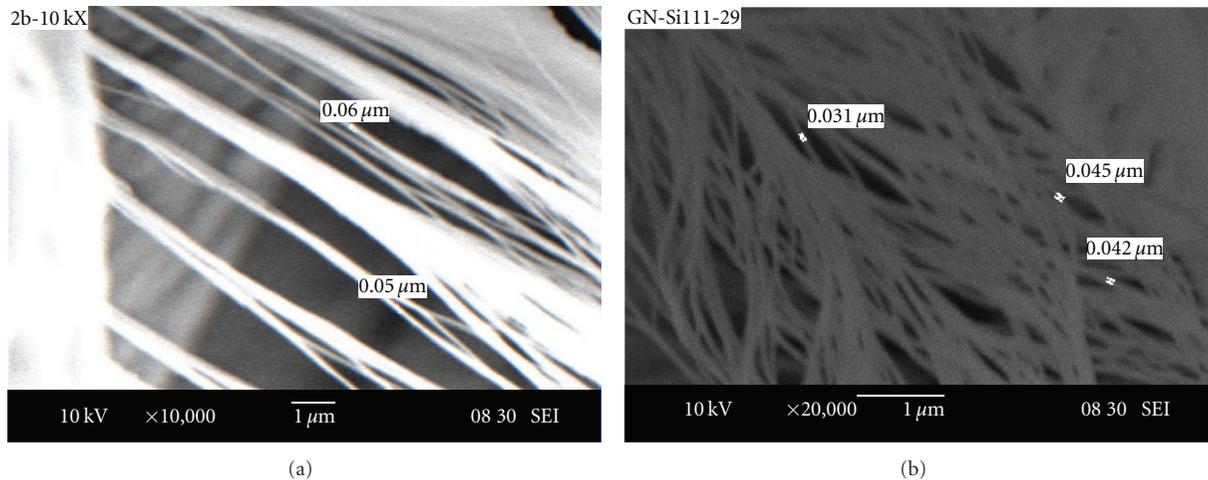


FIGURE 1: SEM images of GaN NWs on (a) PZnO substrate and (b) PGaN substrate.

the substrates were placed in the second boat at a distance of 6 cm from the powder, which was placed in the center of the first boat. Two sets of experiments were conducted. In the first set, porous zinc oxide (PZnO) was used as substrate, and in the second set, porous gallium nitride (PGaN) was used. The size of each substrate was approximately  $1 \times 1 \text{ cm}^2$ ; one substrate was used in each experiment. The Ar flow was 1.5 sccm.

The substrates were first washed and cleaned using the standard RCA cleaning procedure. Next, the substrates were ultrasonically cleaned with acetone and isopropyl alcohol (IPA), rinsed with distilled water, and dried using a nitrogen gas blow system. The temperature of the heating region where the substrates were placed was  $1150^\circ\text{C}$ . A flow of Ar gas was initially used to purify the tube for 15 min before placing the samples into the furnace and introducing back the gas flow into the system. The furnace was turned off to allow it to cool to room temperature. The samples were removed from the furnace after 20 min.

The structures of the as-grown samples were then characterized by a scanning electron microscope (SEM, JEOL JSM-6460LV) operated at 10 kV and by transmission electron microscope (TEM, FEI CM 12) operated at 120 kV. Further structural and optical characterizations were performed using high-resolution X-ray diffraction (HR-XRD), energy-dispersive X-ray spectroscopy (EDX), and room temperature photoluminescence spectroscopy (PL) with He-Cd laser ( $\lambda = 325 \text{ nm}$ ) using a HORIBA JOBIN YVON-HR800 UV microspectrophotometer with a resolution of  $1 \text{ cm}^{-1}$ .

### 3. Results and Discussion

The SEM images in Figures 1(a) and 1(b) illustrate the growth distribution of the NWs on the PZnO and PGaN substrates, respectively. The diameters of the wires were approximately 50–60 nm for the samples on PZnO, whereas the diameters for GaN NWs on PGaN (approximately 30–40 nm) were less than those on the PZnO.

For TEM observation, the GaN NWs were pulverized in ethanol 100% and then dispersed onto a copper grid. In Figures 2(a) and 2(b), the TEM images of GaN NWs clearly confirm that the average diameters of the NWs on PGaN were less than those on the PZnO.

TEM images reveal that the geometrical shape of the GaN nanostructures is similar to a wire. Also these images illustrate uniform diameter sizes. Careful TEM observation indicates that all NWs are composed of only one layer of sheet growing along the wire axis, as shown in Figure 2. Moreover, this figure indicates that there is no difference in thickness between the center and edges.

Perfect one-dimensional growth is preferable for using in most device applications, such as solar cells. For example, twinning, stacking faults, and high-order grain boundaries are frequently observed in GaN NWs, and these high-density defects are believed to play an important role in the unidirectional formation and growth of the GaN NWs [11, 12]. Also the growth direction of the NWs is important because the orientation of the NWs is related to their properties [11].

EDX microanalysis of the samples grown on PZnO, shows Zn, O, Ga, N, and Si atoms (Figure 3(a)). However, Figure 3(b) shows EDX analysis of the NWs grown on PGaN, which indicates the presence of Ga, N, Si, and O atoms among which Si and O are from the Si substrates and the oxide layer. For the PGaN, silicon molecules diffused into the GaN porous structure and replaced the position of Ga, which decreased the crystallization temperature of GaN [13]. At high temperatures ( $T > 900^\circ\text{C}$ ), Si tends to remain at Ga sites and acts as donor [14]. A thin layer of silicon oxide was detected in the interface between GaN and the Si wafer. The diffusion of oxygen during deposition into Si wafer caused the formation of silicon oxide. No other impurities were detected. For the two samples grown on both PZnO and PGaN, wurtzite GaN has a higher Si content and a lower Ga and N content.

Figure 4 shows typical room-temperature PL spectra of the GaN NWs with He-Cd laser used as an excitation source

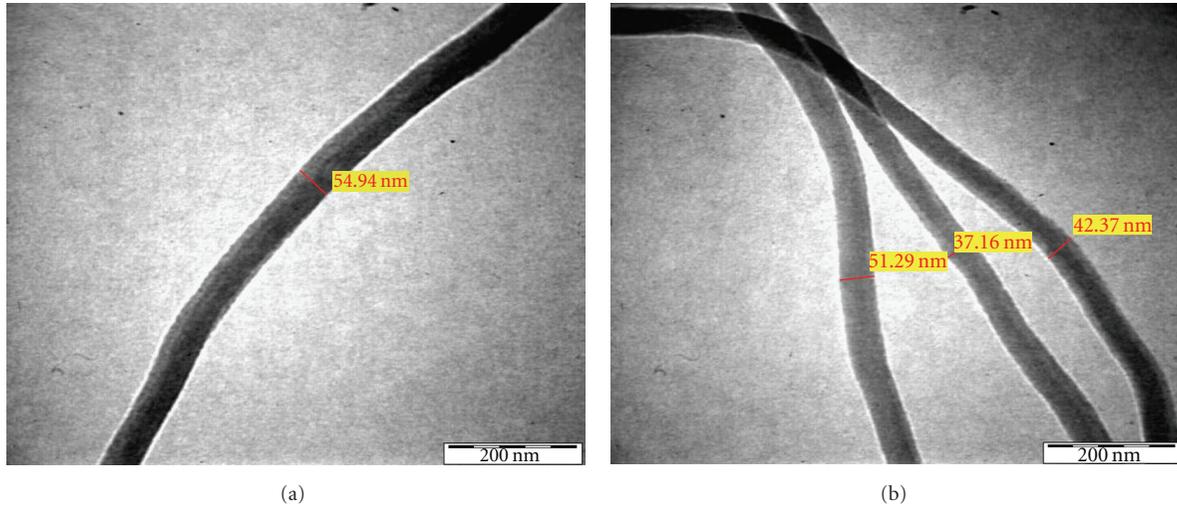


FIGURE 2: TEM images of GaN NWs on (a) PZnO substrate and (b) PGaN substrate.

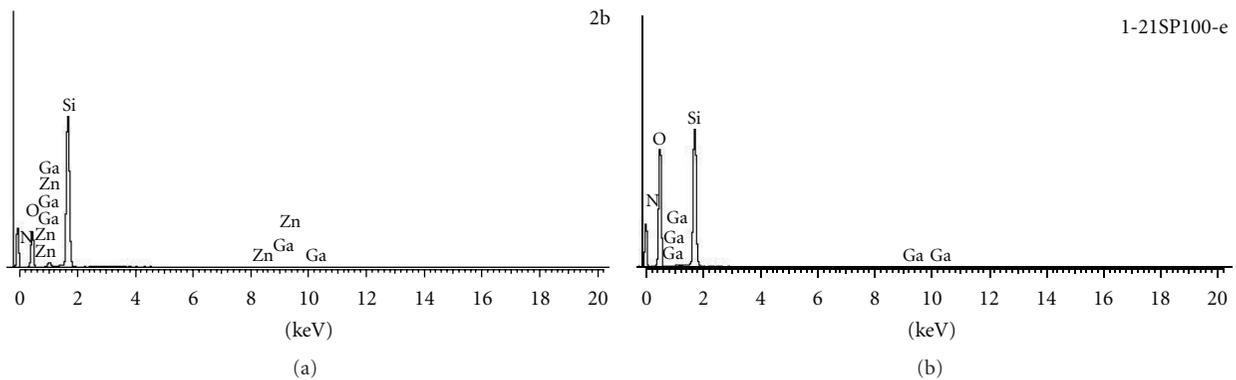


FIGURE 3: EDX spectra of GaN NWs on (a) PZnO substrate and (b) PGaN substrate.

(325 nm wavelength). Figure 4(a) shows a dominant broad peak of as-grown PZnO located at 369.8 nm, and Figure 4(b) shows the PL peak of GaN NWs on PZnO at 368.4 nm. These peaks represent band-to-band recombination in GaN NWs. The as-grown PZnO shows prominent green emission lines. The green emission lines were essentially caused by the defects that resulted during ZnO porous fabrication [15].

Figures 4(c) and 4(d), respectively, show that the dominant broad peak of as-grown PGaN is located at 352.9 nm and that of the GaN NWs on PGaN is at 362.8 nm. No other peaks were found in the PL spectra, indicating that the as-synthesized GaN nanostructures have good optical quality and few defects. Focusing on the PL of the GaN NWs shows that, on the surfaces of the PZnO and PGaN, there are fibrous NW structures that can increase the number of luminescent centers which can increase the PL of the GaN NWs due to additional electron-hole pairs formed for recombination.

The broadening of the energy bandgaps at 368.4 nm (3.37 eV) and 362.8 nm (3.42 eV) for GaN NWs on PZnO and PGaN, respectively, is due to quantum confinement effects of the NWs crystalline structure and different degree

of quantum confinement in different GaN NWs that affects the electron-hole pair recombination [16].

The GaN NWs show a very good emission property, which is a great advantage for laser device applications. Comparing the PL of GaN nanostructure on both porous substrates to the PL spectrum of the as-grown substrate shows that the intensities of the GaN NWs peaks are significantly less than the intensity of the PL peaks of their as-grown substrates. The decrease in intensity of these peaks during annealing to produce GaN NWs is due to diminishing atomic ordering with heating.

Figure 5 shows the HR-XRD spectra of the as-grown PZnO, PGaN, and GaN NWs grown on PZnO and PGaN. The rather sharp peaks can be indexed to the hexagonal wurtzite structure of GaN NWs with lattice constants  $a/b = 3.1350 \text{ \AA}$  and  $c = 5.1190 \text{ \AA}$ . These values are close to the reported values of bulk GaN crystals [17].

Figures 5(a) and 5(b) show the X-ray diffraction patterns of the as-grown PZnO and PGaN wafers, respectively. These figures confirm the formation of hexagonal wurtzite porous ZnO and Porous GaN. Figure 5(a) shows two peaks attributed to PZnO: higher intensity (0002) and lower

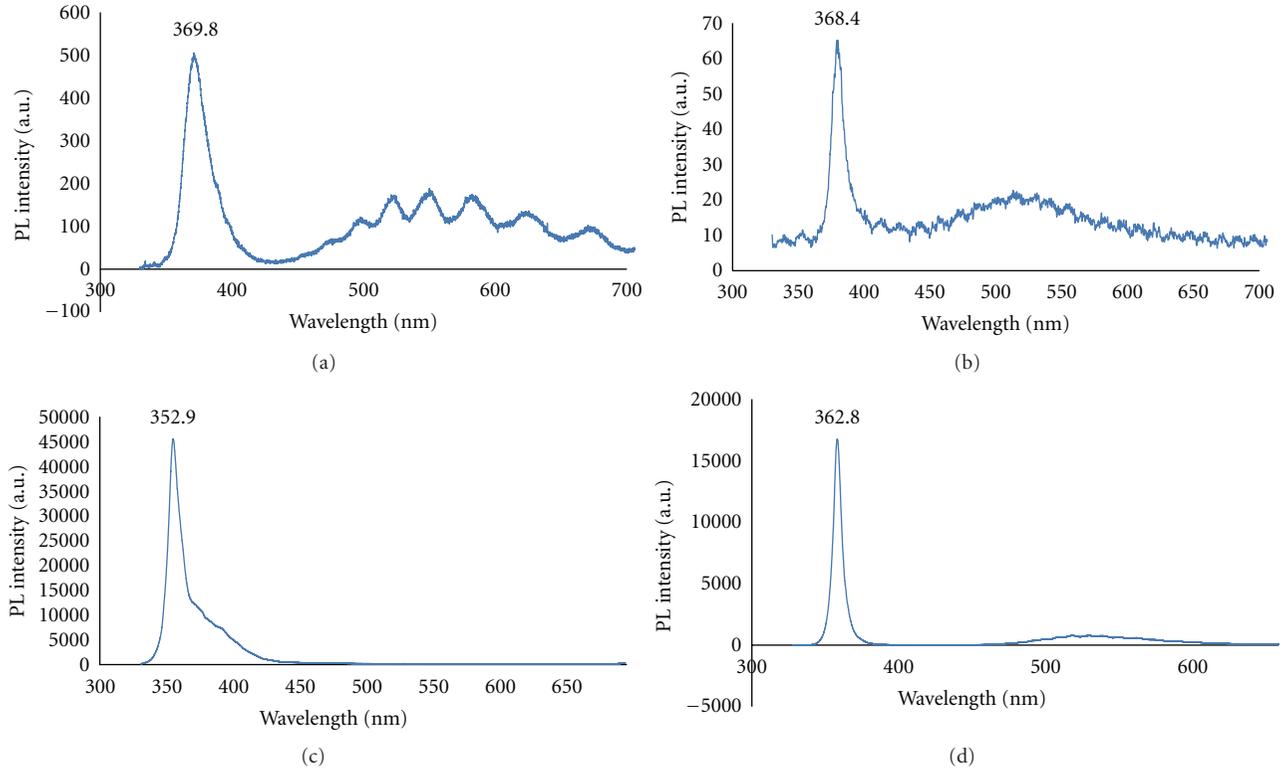


FIGURE 4: PL spectrum of the (a) as-grown PZnO, (b) GaN NWs on PZnO, (c) as-grown PGaN, and (d) GaN NWs on the PGaN substrate at room temperature (300 K).

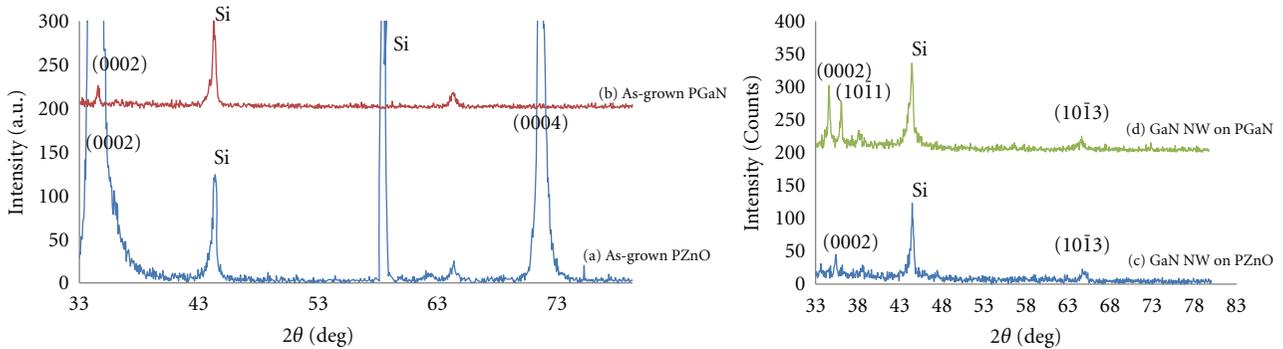


FIGURE 5: X-ray diffraction of the as-grown (a) PZnO and (b) PGaN wafers and X-ray diffraction of the GaN NWs (c) on PZnO substrate and (d) on PGaN substrate.

intensity (0004). This XRD spectrum mainly shows the ZnO porous (0002) diffraction peak at  $2\theta = 34.3^\circ$ , whereas Figure 5(b) shows a (0002) higher diffraction peak at  $2\theta = 34.5^\circ$  for PGaN.

Figure 5(c) shows a typical HR-XRD pattern of the GaN NWs deposited on the PZnO and confirms the formation of single-crystal GaN NWs. The XRD spectrum mainly shows the GaN NWs (0002) diffraction peak at  $2\theta = 35^\circ$ , with full width at half maximum (FWHM) intensity of  $0.246^\circ$  of the hexagonal wurtzite-type structure.

Figure 5(d) shows another XRD pattern of the GaN NWs deposited on the PGaN. Three peaks are attributed to the GaN NWs: higher (0002), lower (1011), and the lowest

(1013). The XRD spectrum mainly shows the GaN NWs' (0002) diffraction peak at  $2\theta = 35^\circ$ , with FWHM intensity of  $0.1968^\circ$ .

No diffraction peaks from  $\text{Ga}_2\text{O}_3$  or other crystalline impurities could be detected in the samples, which indicate that the samples are of high purity. More GaN NW peaks can be observed on the PGaN substrate than on the PZnO substrate. This indicates the higher quality of the NWs on the PGaN. PGaN has no mismatch with the GaN NWs, making NW formation more pliant than those on PZnO (lattice mismatch between GaN and ZnO is 1.8%) [18]. Therefore, the XRD spectrum of the NWs on PGaN shows greater number of peaks with higher intensity.

Considering the SEM images of these NWs, the ratio of the length of the NW ( $>10\ \mu\text{m}$ ) to its width ( $\sim 40\ \text{nm}$ ) shows that the growth rate in the [0001] direction is nearly 250 times faster than that of all other directions [19].

It can be suggested that, under the Ar gas flow (1.5 sccm), the GaN vapor is supersaturated and has a rather small average mean free path. Whenever small crystalline nuclei of GaN NWs are formed, GaN molecules prefer to very quickly self-assemble in the (0001) plane. This kind of preferred one-dimensional growth suggests that the growth pattern corresponds to the fastest way of reducing the system free energy under present nonequilibrium reaction conditions, which means that Ga-N dimer has the most stable structure in the (0001) surface.

If the growth process was conducted in vacuum, the peak intensity would be much better than those obtained in this experiment [20]. The results from the XRD spectra analysis reinforce the conclusions derived from PL and morphological studies and confirm that the formation of GaN NWs on PGaN is better than that of GaN NWs on PZnO.

#### 4. Conclusions

High-density GaN NWs were synthesized on porous PZnO and PGaN substrates by thermal evaporation method GaN using commercial powder. Thermal evaporation technique is a promising and inexpensive technology for producing GaN NWs, of which the size and distribution can be controlled by changing the growth conditions [4], the size and the porosity of the substrate, duration of growth, and gas flow.

SEM and TEM images show that the diameters of the GaN NWs are in a good range of NWs. The smaller or bigger value of the NW diameter in the case of in-pore growth likely results from the deposition of GaN on the pore walls at temperatures above  $1000^\circ\text{C}$  [21]. The morphology of the synthesized NWs reveals that porous substrates play important roles in the fabrication of GaN nanostructures [22]. The quality of grown GaN NWs for different substrates is highly dependent on the lattice mismatch between the NWs and their substrates.

Results indicate that NWs grown on PGaN have better quality and higher density compared with NWs on PZnO. Structural and optical characterizations by EDX, XRD, and PL show that the growth of the NWs was a function of the semiconductor materials of the porous substrate.

The XRD and EDX spectra show that the NWs are of single-crystal quality with hexagonal wurtzite GaN structure and have preferential [0001] growth direction. PL spectra of the GaN NWs at room temperature show broad and high-intensity peak emissions, which indicate that the NWs are of relatively good crystalline and optical quality.

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