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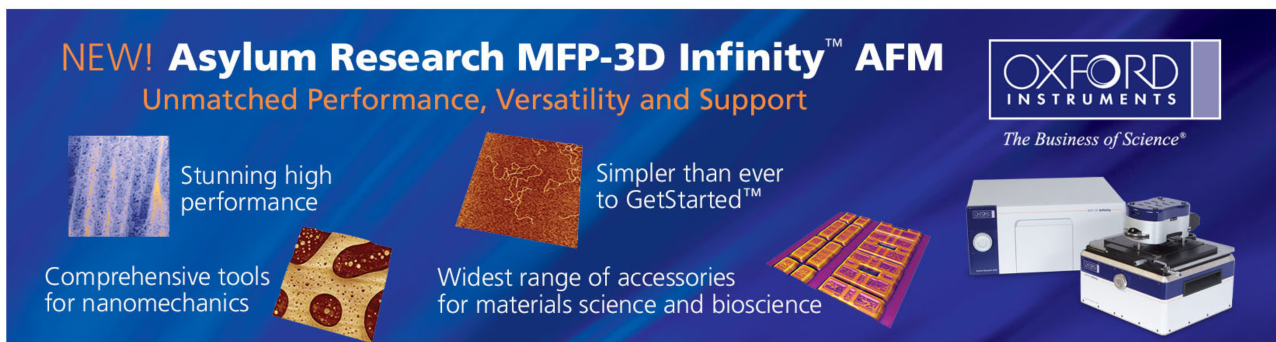

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Freestanding high quality GaN substrate by associated GaN nanorods self-separated hydride vapor-phase epitaxy

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This work proposes a method for fabricating 2 in. freestanding GaN substrates of high crystallographic quality and low residual strain. Arrays of GaN nanorods with sidewalls coated with silicon dioxide (SiO_2) were randomly arranged on the sapphire substrate as a growth template for subsequent hydride vapor-phase epitaxy (HVPE). The passivation of the sidewalls coated with SiO_2 prevents the coalescence of GaN grains in spaces between the rods, causing them to grow preferentially on the top of individual rods. The proposed method significantly improves GaN crystal quality and results in self-separation from the underlying host sapphire substrate due to the relaxation of thermal strains in the HVPE cooling-down process. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3195684]

Recently, GaN-based materials have attracted much interest because of their wide range of applications, such as in light-emitting diodes and laser diodes. Unfortunately, a major issue in the production of blue-violet optoelectronic devices is the lack of a readily available substrate for the growth of GaN films of high crystallographic quality. Although several attempts have been made to solve this problem, the most promising approach is to seed a freestanding GaN substrate from a sacrificial substrate. However, despite the successful demonstration of a freestanding GaN substrate using hydride vapor-phase epitaxy (HVPE) by several groups,[1] some critical problems remain to be solved, such as the formation and the control of dislocation defects, the appearance of residual-strain-induced cracks in the thick GaN film, and the bowing of freestanding films caused by the large mismatch between the grown GaN film and the host substrate.[2] A void-assisted separation technique was recently presented for forming a full-size (45 mm in diameter) self-separated GaN substrate, involving the formation of a TiN nanonet on the surface,[3] but the surface morphology after the TiN treatment is difficult to manipulate. Kusakabe *et al.*[4] studied the growth of freestanding GaN film on sapphire substrates by rf-plasma assisted molecular beam epitaxy. The unstrained GaN layers are employing self-organized GaN nanocolumns which involve an air gap structure as a footing layer of overgrown GaN. This work demonstrates an approach for realizing a freestanding GaN substrate with high crystal quality and nearly no residual strain. The selective growth of arrays of nanorods whose sidewalls are coated with SiO_2 is identified and utilized to form a compliant layer to decouple the effect of the lattice mismatch from the thermal expansion of the 300 μm overgrown GaN layer and the host sapphire substrate. During the cooling process in HVPE, the 300-μm-thick freestanding GaN substrate was self-separated because of the small conjoined area of the top surfaces of the nanorod arrays. Further examination of optical properties reveals that the freestanding GaN substrate herein not only emits an intense photoluminescence (PL) signal, but also is free of cracks and residual strains in the crystal structure.

Figure 1(a) shows the proposed process of fabrication of the GaN substrate. In the beginning, we grew an undoped 1.8-μm-thick GaN layer on a 2 in. *c*-plane sapphire substrate by metal-organic chemical vapor deposition (MOCVD). Then, a 500-nm-thick SiO_2 layer was deposited on the MOCVD-grown GaN layer by plasma-enhanced chemical vapor deposition, followed by a 20-nm-thick Ni layer deposited by an e-gun evaporator. The sample was then annealed at 850 °C for 90 s in nitrogen ambient to form self-

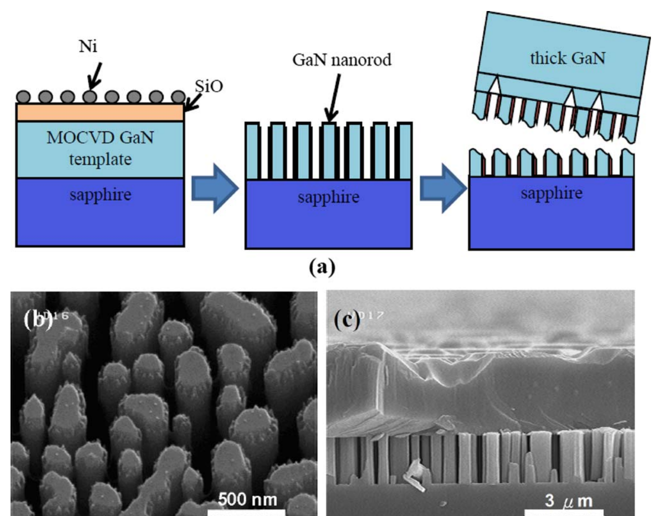

FIG. 1. (Color online) (a) Schematic process flowchart for GaN nanorods, (b) SEM image of GaN nanorod arrays with SiO_2 passivated sidewalls, and (c) cross-sectional SEM image for the initial stage of HVPE regrowth with a growth time of 2 min.

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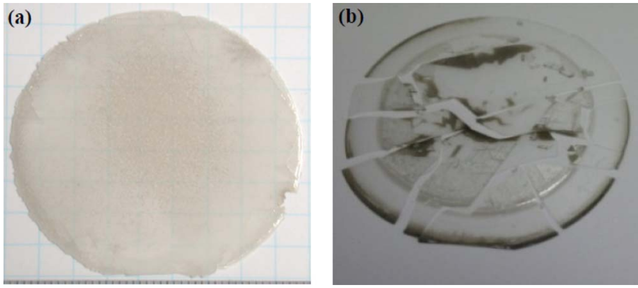

FIG. 2. (Color online) Results of GaN thick films obtained from (a) GaN nanorod arrays and (b) flat GaN surface.

assembled Ni nanoclusters on the SiO_2 layer. The Ni nanoclusters acted as etching masks and subsequently, the reactive ion etching (RIE) and inductively coupled plasma dry etching were performed in sequence to form GaN nanorod arrays.[5] After etching, the GaN nanorod arrays were dipped into heated HNO_3 and buffered oxide etchant to remove the residual Ni and SiO_2 from the top of the arrays. The diameter and the etched depth of the nanorods were 200–500 nm and 1.8 μm, respectively. Afterward, we again deposited a 200-nm-thick SiO_2 layer on the nanorod template and then utilized RIE to remove the SiO_2 layer on the top surfaces of the GaN nanorods, as shown in Fig. 1(b). This figure clearly exhibits the sidewalls of GaN nanorods were surrounded by a thin SiO_2 layer with a thickness of $\sim$40 nm. Finally, HVPE was used to regrow a 300-μm-thick GaN layer; the details of the HVPE process are described elsewhere.[6] During the HVPE cooling process, the 300-μm-thick GaN substrate self-separates from the underlying host sapphire substrate as a result of the release of thermal strain. For comparison, a conventional as-grown GaN substrate was also prepared by HVPE on sapphire substrate. Figure 1(c) shows the cross-sectional scanning electron microscopy (SEM) image of the initial regrowth stage of HVPE. In this figure, the thickness of the GaN bulk is approximately 3.3 μm and the surface is quite rough. The rough surface is believed to be associated with different growth rates of GaN seeds in the initial stage of HVPE. This problem is solved by increasing the growth time. Unlike in the growth of GaN on microscale patterned substrates,[7] no void was observed in this work because the GaN rod-to-rod intervals were small enough (200–400 nm).

Figures 2(a) and 2(b) show the results of as-grown 300 μm GaN films separated from GaN nanorod-array template and flat GaN template, respectively. In Fig. 2(a), a complete 2 in. self-separated freestanding GaN substrate was demonstrated. According to Fig. 1(c), we can observe that the GaN regrowth layer was suspended on the nanorod-array template because of the SiO_2 sidewall passivation. In general, during HVPE cooling process, the large thermal stress will be induced by the quiet different thermal expansion coefficient between GaN and Al_2O_3. In order to release the thermal stress during HVPE cooling process, the GaN nanorods were broken and resulted in the self-separation of GaN from sapphire substrate. In contrast, as shown in Fig. 2(b), the GaN grown on flat GaN smashed into several pieces because the thermal stress cannot be released in the HVPE cooling process.

Figures 3(a) and 3(b) show the analysis of Nomarski images for the GaN substrate separated from the nanorod-

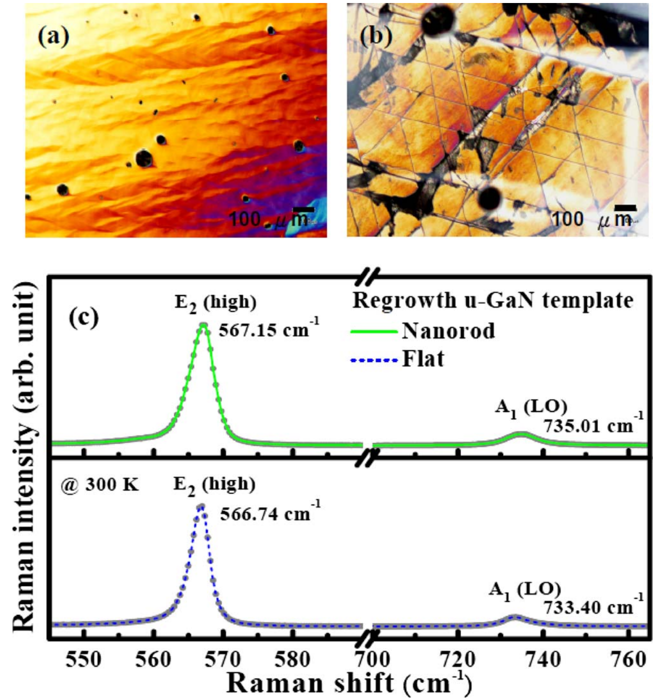

FIG. 3. (Color online) Optical microscope images under the Normarski illumination for GaN thick films obtained from (a) GaN nanorod arrays and (b) flat GaN surface. (c) Cross-sectional Raman scattering analysis of GaN thick films obtained from GaN nanorod arrays and flat GaN surface.

array template and flat GaN template, respectively. Comparing with Fig. 3(a), a large amount of cracks was observed in Fig. 3(b). These cracks were motivated mainly by the influence of tensile stresses and thrived once the critical thickness for GaN grown on the flat GaN substrate was reached.[8] In other words, the absence of cracks in the thick GaN film in Fig. 3(a) implies that the whole growth process is with low tensile stress. Some large, about 10–84 μm in diameter, and sparse hexagonal pits with six triangular {1011} facets was observed at the GaN surface in Fig. 3(a). Basically we believed it comes from the extremely high growth rate about 200 μm/h and a smoother surface could be achieved under a slower growth condition.

In order to further identify the difference stress in these two samples, we performed the measurement of cross-sectional Raman scattering analysis. The E_2-high phonon modes of GaN substrates obtained from the nanorod-array template and flat GaN template were located at 567.15 and 566.74 cm^{-1}, respectively, as shown in Fig. 3(c). The E_2-high peak for the substrate obtained from the nanorod-array template was very close to that of the stress-free GaN substrate, which is believed to be $567.1 \pm 0.1\ cm^{-1}$.[9] Therefore, the residual stress in the substrate obtained from the nanorod-array template was negligible. The residual stress could be calculated by the following equation:

$$\Delta\omega_\gamma = \omega_\gamma - \omega_0 = K_\gamma \cdot \sigma_{xx},$$

where ω_γ and ω_0 represent the Raman peaks of GaN from flat surface and nanorod-array templates, respectively. The estimated value of stress is about 0.160 GPa by adopting a theoretical K_γ value of 2.56 cm^{-1}/GPa reported by Wagner and Bechstedt.[10] The great difference in stress between these two samples is due to relaxation of the thermal stress, which is inherently accumulated during HVPE regrowth process.

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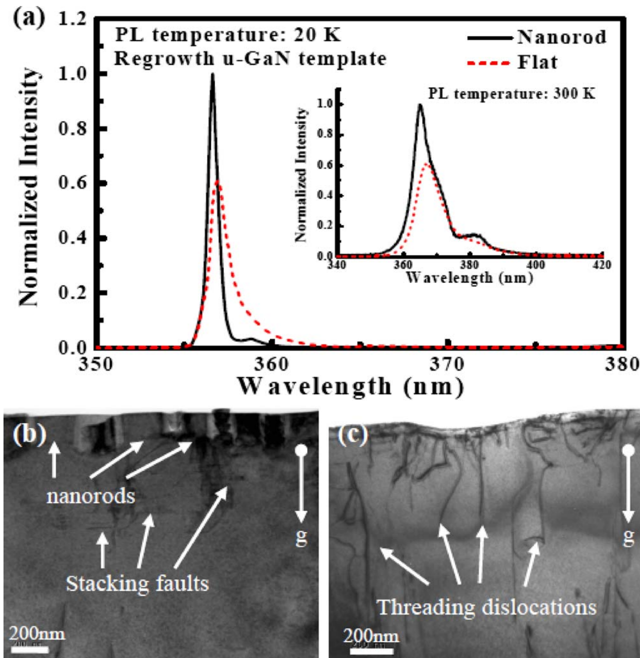

FIG. 4. (Color online) (a) PL spectra of GaN substrates separated from GaN nanorods and flat GaN surface at 20 K. Inset shows the spectra at room temperature. Cross-sectional TEM images for the GaN substrates grown on (b) GaN nanorods and (c) flat GaN surface.

Moreover, we examine the optical properties of these two samples. The 325 nm He–Cd laser was used to perform the PL measurement and laser's output power was set constantly to be 10 mW with a diameter of 100 μm. Figure 4(a) shows the PL spectra (corresponding emission peak energy) at 20 K for the GaN substrate obtained from the nanorod-array and flat GaN template. Their emission peaks are located at 356.62 nm (3.477 eV) and 357.01 nm (3.473 eV), respectively. In comparison with the substrate obtained from the flat GaN template, the PL intensity for the substrate obtained from the nanorod-array template was enhanced by a factor of 1.66, and simultaneously the PL wavelength exhibited a blueshift of about 0.39 nm (3.8 meV). Also, its full width at half maximum (FWHM) is 4.717 meV, which is nearly a half of that obtained from the flat GaN template (7.875 meV). The inset in Fig. 4(a) shows the room temperature PL result. From the inset, the PL intensity was enhanced by a factor of 1.72, and simultaneously the PL wavelength exhibited a blueshift of about 2 nm as compared to that of the substrate obtained from the flat GaN template. Besides, a high resolution x-ray diffractometer (XRD) (Bede D1) with a Cu target was employed to investigate the crystalline quality of GaN substrates. The XRD peaks FWHM values are 196.3 in symmetric (002), and 152.9 arc sec in asymmetric (102) axis for nanorod-arrays template, and 350 and 227 arc sec in symmetric and asymmetric axis for flat template sample. We note the number of flat sample is similar to previous flat results[11] and it is not surprising a low number is achieved from nanorod-array sample than flat one since the better crystal quality.

Regarding the emission wavelength, it is well known that a residual strain in the semiconductors would affect the energy band gap and then result in a shift in emission wavelength. In general, the type of induced stress could be identified from the blueshift or redshift in emission wavelength. For the GaN grown on the sapphire substrate, a tensile strain was expected to be induced due to its relative small lattice constant than that of sapphire underneath. In Fig. 4(a), therefore, we can consistently observe a blueshift for the sample from nanorod arrays in both 20 K and room temperature PL measurement. In addition to the measurement of Raman scattering, it is another solid evidence that our proposed scheme can provide a GaN substrate which is free of residual strain. On the other hand, the high threading dislocation density (TDD) existing in GaN plays the roles of nonradiative recombination centers to deteriorate the luminescence efficiency.

Figures 4(b) and 4(c) show the typical bright field cross-sectional transmission electron microscopy (TEM) images of GaN substrate obtained from the nanorod-array and flat GaN template, respectively. In contrast with Fig. 4(c), we found that a number of stacking faults often occurred above the GaN nanorods as shown in Fig. 4(b), where visible threading dislocations (TDs) were rarely observed in the vicinities. It is believed that the presence of stacking faults could block the propagation of TDs.[12] From the TEM images, the TDD in the substrate obtained from nanorod arrays and flat GaN template is estimated to be $\sim 10^7$ and $\sim 5 \times 10^9$ cm^{-2}, respectively.

In summary, we have the GaN nanorod arrays with SiO_2 sidewall passivation were utilized to grow the 300-μm-thick GaN substrates. The measurement of E_2-high mode in Raman spectroscopy shows there is no residual tensile stress in the freestanding GaN substrate separated from the nanorod-array template. In addition, the PL spectra exhibited that PL intensity, which is probably attributed to the effective suppression of TTD via nanorod-array lateral overgrowth.

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