



Modulation of Electrical Conductivity and Lattice Distortions in Bulk HVPE-Grown GaN

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The nature of self-organized three-dimensional structured architectures with spatially modulated electrical conductivity emerging in the process of hydride vapor phase epitaxial growth of single crystalline n-GaN wafers is revealed by photoelectrochemical etching. The amplitude of the carrier concentration modulation throughout the sample is derived from photoluminescence analysis and the localized heterogeneous piezoelectric response is demonstrated. The formation of such architectures is rationalized based on the generation of V-shaped pits and their subsequent overgrowth in variable direction. Detailed structure analysis with respect to X-ray diffraction and transmission electron microscopy gives striking evidence for inelastic strain to manifest in distortions of the $P6_3mc$ wurtzite-type structure. The deviation from hexagonal symmetry by angular distortions of the β angle between the basal plane and c-axis is found to be of around 1° . It is concluded that the lattice distortions are generated by the misfit strains originating during crystal growth, which are slightly relaxed upon photoelectrochemical etching.

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Over the last 20 years GaN has become one of the most important semiconductor materials and may replace Si in many electronic applications. Particularly, it is already replacing Si in LDMOS radio-frequency devices used in base stations for mobile communication as well as GaAs for radar applications.¹⁻⁷ The highly advantageous properties of GaN-based semiconductors such as high electron mobility and saturation velocity, high sheet carrier concentration at heterojunction interfaces, high breakdown field, and low thermal impedance make them extremely promising for high-power high-temperature microwave applications, as evidenced by their high Johnson's figure of merit.⁸⁻¹⁰ Exemplary, solid-state lighting optoelectronic devices assembled from white LEDs based on GaN are replacing conventional light sources such as incandescent bulbs and fluorescent lamps nowadays. This is due to their high efficiency, long operational lifetime, compact form factor, no emission of harmful ultraviolet (UV) or infrared radiation, and low maintenance cost. A recent review also highlights the prospects of GaN LEDs for visible light communications (VLC) in both fiber and free-space embodiments.¹¹ The state-of-the-art technology enabling bandwidth of GaN LEDs in the range of >400 MHz has been explored and multi-gigabit-per-second VLC has been demonstrated.

Better performance characteristics than those of Si power devices make also GaN power devices promising for automotive applications.¹² These electronic applications are based on using primarily silicon or silicon carbide substrates, since from a synthesis point of view thick GaN substrates are commercially unavailable. In spite of considerable progress in addressing the challenges related to significant mismatches between crystal lattices and thermal expansion coefficients, as well as silicon thermal stability when using Si substrates,¹³ GaN-on-Si, GaN-on-SiC, and GaN-on-Sapphire remain costly solutions. In fact, GaN remains the most costly electronic material among the wide bandgap compounds (excluding single crystalline diamond).

For a long time, GaN has been grown by Metalorganic Chemical Vapor Deposition (MOCVD) on sapphire, Si, or SiC for research

and device applications. However, challenges related to the growth of high-performance films remain, still hampering their utilization in devices.¹⁴ Therefore, single crystalline GaN substrates are essential for future high-performance devices.

Nowadays, there are three main technologies used for GaN crystal growth: hydride vapor phase epitaxy (HVPE), sodium flux, and ammonothermal growth.¹⁵ The last two approaches belong to the group of solution growth methods. High structural quality and high purity have been demonstrated by using the sodium flux growth method. However, it is supposed that this method is a perfect technology for fabricating seeds for further growth of gallium nitride but not for mass production of crystalline wafers, because this technological process is quite expensive and complicated.¹⁵ On the other hand, the ammonothermal growth seems to be appropriate for mass production of GaN crystals, high structural quality substrates with 2-inch diameters and various electrical properties being successfully grown.¹⁶ However, the main problem of this technology is the low growth rate of up to a few micrometers per hour. Apart from that, despite the high crystalline quality, the properties of ammonothermal GaN crystals and substrates are affected by the presence of impurities and other defects that hinder their use for device applications.¹⁷ Therefore, the most appropriate approach for manufacturing GaN substrates is considered HVPE, due to the relatively high growth rate (>100 $\mu\text{m/h}$) and crystallization of high-purity material.¹⁵ In spite of important advantages of this technology, however, achieving a good crystalline quality is still challenging, because of the formation of V-shaped defects or pits, which lead to the formation of extended inhomogeneous structures upon subsequent overgrowth (see for example Refs. 18,19). Self-organized 3D nanostructured architectures including quasi-ordered concentric hexagonal structures generated during the growth of single crystalline n-GaN substrates by HVPE have been revealed by subjecting the samples to electrochemical or photoelectrochemical (PEC) etching.¹⁸ It was supposed that these architectures are produced due to a fine modulation of doping related to the spatial distribution of impurities in the volume of samples generated by some peculiarities of the HVPE growth.

In this paper, we demonstrate by means of transmission electron microscopy (TEM) that the self-organized nanostructured architectures disclosed by photoelectrochemical etching are not related to systematic variations of the crystal structure but by the modulation

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