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Formation of large-area freestanding gallium nitride substrates by natural stress-induced separation of GaN and sapphire

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Abstract

This paper addresses the formation of freestanding GaN substrates by a natural separation mechanism, effectively eliminating the need for post-growth processes such as laser liftoff, chemical etching or mechanical lapping to form freestanding GaN substrates. A number of GaN thick films were grown onto sapphire substrates by the hydride vapor-phase epitaxy (HVPE) method with thickness varying from 200 μm to 3.8 mm using either a low-temperature GaN or an AlN buffer as the nucleation step. We have found that samples grown on a low temperature GaN buffer naturally delaminate from the sapphire substrate post-growth over the entire thickness range studied. Furthermore, we have observed that the thinner films have high crack densities leading to the delamination of several smaller freestanding pieces. As the GaN thickness increases, the area of the delaminated pieces also increases, ultimately leading to a 1-to-1 correlation between initial sapphire substrate area and freestanding GaN area. However, the GaN films grown on AlN buffers did not delaminate. These results were accounted for by calculating the thermal stresses in the GaN film and substrate as a function of film thickness using Stoney's equation and assuming that the GaN buffer undergoes decomposition at the growth temperature.
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1. Introduction

The progression of nitride semiconductor technology has been rapid with a plethora of devices having been demonstrated to date. The majority of work in this field has been carried out on non-native substrates, predominantly *C*-plane sapphire and 6H silicon carbide due to the commercial unavailability of gallium nitride (GaN) substrates [1]. Such substrates are not ideal for the growth of GaN due to large mismatches in lattice constants and thermal expansion coefficients leading to high dislocation and crack densities in the epitaxial layers. Thus far, the increase in the performance metrics of nitride-based devices has relied on advancements in the hetero-epitaxial growth of such materials including the use of nitrididation (in the case of growth on sapphire) and optimized buffer layers [2,3], as well as more exotic techniques such as lateral epitaxial overgrowth [4] and dislocation filtering layers [5]. While these techniques allow for the growth of device quality GaN, it is commonly believed that the successful development of the next generation of GaN-based devices relies inexorably on the availability of high quality GaN substrates. Such substrates would allow device growth to take place homoepitaxially, which has a number of benefits. Of paramount importance is the markedly lower dislocation densities that can be realized in device structures grown homoepitaxially onto low dislocation bulk GaN substrates, allowing for higher carrier mobilities [6], increased radiative recombination efficiency [7], longer device lifetime [8], and lower leakage current [9,10]. The matching of thermal expansion between epitaxial layer and substrate is also realized and thus eliminating the associated thermal stress, which is a significant source of cracking. The availability of such substrates yields several additional advantages in the arena of device processing.

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Since GaN substrates can be made electrically conductive, the processing of certain device structures would be made simpler by enabling the deposition of metal contacts onto the substrate, eliminating the need for an etching step to contact underlying device layers. GaN's relatively high thermal conductivity also allows for efficient heat sinking of devices grown on such substrates without the need for flip–chip bonding. And lastly, homoepitaxial layers generally follow the same orientation as the substrate, allowing for the matching of cleavage planes, which becomes important when one desires to cleave facets for lasers. Given the many virtues of homoepitaxial growth, it is abundantly clear why there is a great deal of motivation to develop GaN substrates.

Currently, there are a number of articles that address the formation of freestanding GaN substrates. Owing to the technological difficulties of GaN growth from the liquid phase, the hydride vapor-phase epitaxy (HVPE) method has emerged as the front-running candidate for the commercialization of such substrates due to its high growth rates and relatively low cost. By this method, the formation of freestanding bulk GaN is preceded by the heteroepitaxial deposition of a thick layer of GaN onto an appropriate substrate and a separation step to free the bulk GaN from its substrate. With regards to separation of film and substrate, researchers have employed a number of techniques including mechanical lapping [11], chemical etching [12], laser liftoff [13], and void assisted separation [14]. Each of these methods, however, requires ex situ processing of the substrate either before or after the growth. This paper addresses the growth of crack-free bulk freestanding GaN by the HVPE method, whereby separation occurs naturally post-growth and all required steps are performed within the same reactor, effectively streamlining the process. The paper addresses the issues related to the suppression of crack formation, as well as the mechanism that allows for natural separation to occur.

2. Experimental methods

The HVPE method was used to grow the materials in this study. The reactor employed is a home-built cylindrical quartz system operating horizontally within a three-zone furnace. Gallium chloride (GaCl) is synthesized in situ by flowing hydrogen chloride gas (HCl) over a quartz boat containing liquid gallium held at 900 °C in a central tube. Ammonia is flowed in an outer tube, and is appropriately mixed via convective and diffusive means with the GaCl flow prior to impinging onto the substrate where GaN growth takes place. Nitrogen is used as the carrier gas and the reactor is operated at atmospheric pressure. Under the system's current configuration (geometry and flow conditions), growth rates up to 700 μm/h have been established.

A number of GaN films with thickness ranging between 150 μm and 3.8 mm were grown onto *C*-plane (0 0 0 1) sapphire utilizing a two-step growth method. Prior to growth, each wafer was exposed to a flow of GaCl as a surface pretreatment at 1000 °C [15]. The exact influence of this substrate pretreatment step is not well understood. We hypothesize that upon the decomposition of GaCl on the substrate the Ga reacts with physisorbed oxygen to form volatile GaO and Cl reacts with surface carbon to form volatile chlorocarbons. Both of these impurities are undesirable for epitaxial growth. The substrates were then cooled and a low-temperature GaN buffer layer, approximately 100 nm thick, was deposited at 600 °C [2,3]. The substrate was then ramped up to a temperature of 1020 °C at which the bulk GaN film was grown. Post-growth, the cooling rate was dictated by the natural loss of heat from our furnace, with an initial rate of approximately 60 °C/min that gradually declined with the temperature. Some samples were also grown on an AlN buffer, predeposited on a (0 0 0 1) sapphire substrate by the MBE method.

The samples were examined using optical microscopy in reflection mode to image crack densities on the surface of the grown films. While additional cracks may exist in the bulk, it is the surface cracks that we have concerned ourselves with since it is those that will affect further epitaxy.

3. Results and discussion

3.1. Suppression of crack formation

Cracks in a material are initiated and propagated due to stress. The causes of stress are numerous during the heteroepitaxial growth of GaN on sapphire with significant contributions originating from lattice mismatch and island coalescence [16]. These stresses are relieved, to a large extent, through the formation of dislocations, grain boundaries and cracks during the first few microns of growth [17]. Cracks that are generated during the growth may be overgrown and therefore buried within the bulk, resulting in a relaxed epitaxial layer at the growth temperature [17].

Post-growth, the stress that is typically observed is dominated by thermal stress. The act of cooling the sample from the growth temperature to room temperature imparts stress in both the sapphire substrate as well as the GaN layer due to differences in the thermal expansion coefficient between the two materials. Specifically, the average in-plane thermal expansion coefficient in the temperature range 300–1000 K for sapphire ($7.5 \times 10^{-6}\,K^{-1}$) is greater than that of GaN ($5.6 \times 10^{-6}\,K^{-1}$) causing the sapphire to contract at a faster rate than GaN upon cooling [18]. However, the sapphire is mechanically constrained by the GaN epi-layer, and therefore held at a length that is elongated compared to the length it would have achieved had it not been constrained. This results in a tensile stress in the sapphire substrate. The stress analysis of the GaN layer follows analogous logic. GaN would like to contract at a certain rate but is coerced to contract faster than normal under action of the sapphire substrate. The final

length of the GaN layer is shorter than it would be had the layer contracted independently and is thus under compressive stress. Such stresses can be quantified utilizing the Stoney Equation (1), which expresses the thermal stress in the film as a function of fundamental parameters of the film and substrate [19].

$$\sigma_f = \frac{(\alpha_s - \alpha_f)\Delta T}{[(1-\nu_f)/d_f E_f) + ((1-\nu_s)/d_s E_s)](d_f)}. \quad (1)$$

According to Eq. (1), the epitaxial film stress (σ_f) depends on the thermal expansion coefficients (α), Poisson's ratios (ν), Young's moduli (E), thickness (d), and the temperature change (ΔT). The subscripts "f" and "s" denote values for the film and substrate, respectively. Fig. 1 shows the theoretical thermal stress generated as a result of cooling GaN on sapphire from 1025 °C (GaN growth temperature) to 25 °C (room temperature) as a function of the GaN thickness. Table 1 shows the associated material properties used in the calculation of the data of Fig. 1. The values of the thermal expansion coefficient listed in Table 1 are the average values determined from X-ray measurements as a function of temperature [18]. It should be noted that what is plotted in Fig. 1, is the magnitude of the stress and that the nature of the stress in the GaN layer is compressive and that of sapphire is tensile. It should also be noted that this equation does not take relaxation mechanisms such as cracking into account, and thus the actual stress measured for a film will be lower when the predicted stress exceeds the threshold for activating a stress relieving mechanism in either material. This limitation aside, the relevant feature to note in this plot is that the compressive stress of GaN is reduced by over two orders of magnitude as the film thickness increases to 1 mm. Correspondingly, the tensile stress of sapphire increases by over two orders of magnitude in the same range of film thickness.

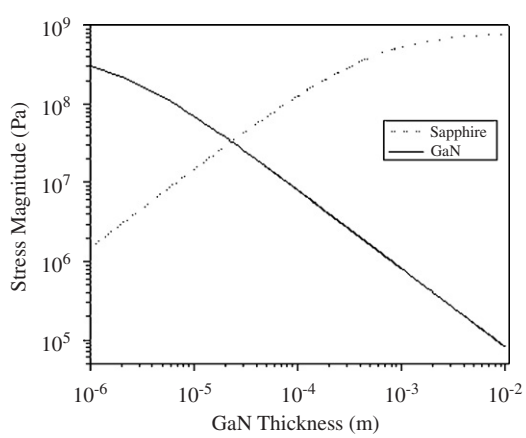

Fig. 1. Calculated thermal stress in sapphire and GaN as a function of GaN deposition thickness.

Table 1
Input parameters to the Stoney equation for thermal stress calculation

Stoney Eq. parameter	GaN	Sapphire
Thermal expansion coeff.	$5.6\times10^{-6}\,K^{-1}\perp c$ [18]	$7.5\times10^{-6}\,K^{-1}\perp c$ [18]
Poisson ratio	0.17 [20]	0.25 [1]
Young's modulus (GPa)	210 [21]	352 [1]
Thickness	Variable	330 μm
$\Delta T = 100$ K		

The mechanisms of post growth cracking of GaN on sapphire substrates are still not very well understood to this day. However, empirical observations in the literature have shown that cracking in the sapphire substrate may initiate cracks in GaN at the interface. It is also shown that cracks, which are overgrown during the growth process, may leave voids within the material as demonstrated from SEM images in Ref. [16]. In the case of the sapphire substrate, one expects it to develop cracks due to the increasing post-growth tensile stress with GaN thickness. In the case of GaN, the large compressive stress presents a problem as well. While cracking is not typically associated with compressive stress failure, compressive stress acts as a driving force for crack propagation in a material with preexisting flaws such as cracks or voids [22]. Uncontrolled buckling and rupture are also unwanted by-products of large compressive stresses. The reduction of such stress in the GaN layer, by means of growing the GaN film very thick, should effectively reduce the propagation of cracks initiated at the GaN/Sapphire interface.

Fig. 2 shows the crack density in three GaN films with thickness of 200, 800 and 1300 μm, grown on low temperature GaN buffers. These data show that the density of surface cracks is reduced as the film thickness increases and specifically the 1300 μm film is free of cracks.

3.2. Separation of bulk GaN layer from sapphire

The preceding discussion on crack formation has yielded conditions under which GaN can be grown crack-free. However, there remains the task of separating the GaN film from the substrate. Post-growth separation techniques such as laser lift-off or mechanical lapping may be employed at this point, but one would ideally like to eliminate such procedures if at all possible to streamline the process.

We have empirically observed that thick GaN films (200 μm +) grown at high temperature (1020 °C) onto a low temperature GaN buffer (deposited at 600 °C) naturally separate from the sapphire substrate upon cooling. This is achieved in a single HVPE reactor without any special processing of the substrate either before or after the growth procedure. Fig. 3 shows a series of such GaN films that have naturally separated. We attribute the observed separation to the low temperature GaN buffer. The GaN buffer layer undergoes decomposition during the high temperature bulk GaN growth. Such decomposition acts to appreciably weaken adhesion at the hetero-interface.

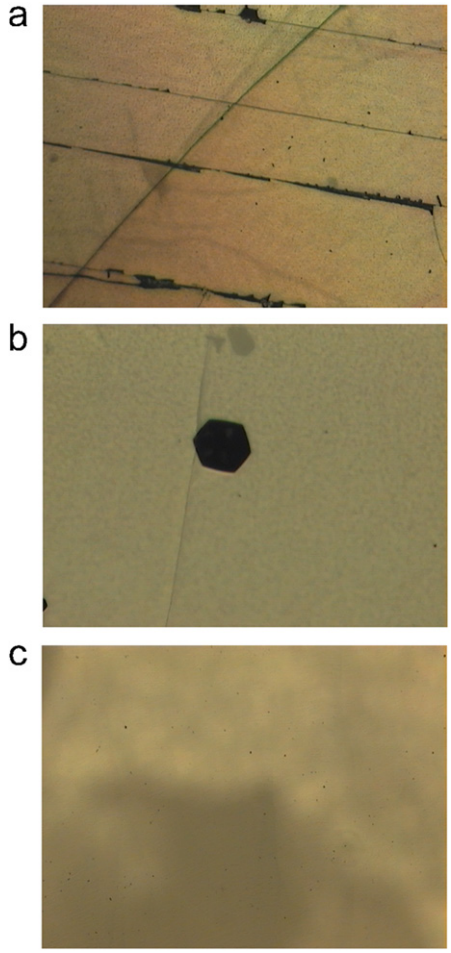

Fig. 2. 800 × 1000 μm optical images of surface crack density for GaN films grown to various thickness: (a) 200 μm film suffers from dense network of cracks separated by 200–300 μm; (b) 800 μm film is sparsely populated with cracks separated by several mm; and (c) 1300 μm film is crack-free.

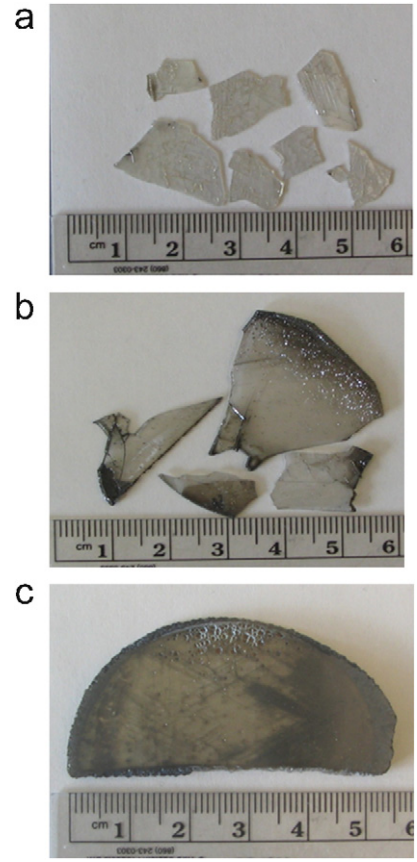

Fig. 3. Freestanding GaN samples post-separation from sapphire substrate with thickness (a) 200μm, (b) 800μm, and (c) 3.8 mm. Initial sapphire dimensions were a 2" wafer for (a) and 1/2 of a 2" wafer for (b) and (c).

Mechanical failure ensues in the buffer layer during the cool down phase on account of thermal stress resulting in the liberation of GaN from the sapphire substrate. Such a process is akin to the void-assisted separation process [14]. In this case, the voids originate from the dissociation of nitrogen in the buffer layer.

The facilitation of separation through the buffer layer is seen as viable explanation to the observed separation based on observations of gallium metal on both the sapphire and GaN side of the once hetero-interface post-separation. Koleske et al. [23] has also demonstrated a stark difference in the decomposition rate of GaN nucleation layers grown at low temperatures (550 °C) and GaN films grown at high temperatures, with measured rates for nucleation layers seen as high as an order of magnitude greater under the same experimental conditions. Further evidence supporting such a mechanism is the failure of GaN films grown under similar conditions onto AlN buffers or directly onto sapphire (without a LT GaN buffer layer) to separate upon cooling. This is due to the higher onset temperature for decomposition of AlN for the former case and the lack of a weakened interfacial structure for the latter.

The size of the liberated freestanding GaN samples in Fig. 3 is shown to increase with the deposition thickness. For thinner films, the GaN is both susceptible to cracking due to thermal stresses as well as complete fracture through the layer during separation due to the inherent fragility of thin materials. Thick films (> 1 mm) bypass both of these problems since they are mechanically sturdy and do not crack under action of the sapphire substrate. As such, one can expect a 1 to 1 correlation between the substrate area and the area of the liberated film. This is demonstrated in Fig. 3(c), where a 3.8 mm thick GaN film separated intact from a sapphire substrate with original dimensions of 1/2 of a 2" wafer.

4. Conclusion

A novel method of generating freestanding GaN has been discussed. We have found that separation of epitaxially grown GaN from sapphire substrates can occur naturally when one employs a LT GaN buffer layer prior to high temperature growth. The enhanced thermal decomposition of the highly defective buffer layer leading

to a severely compromised interfacial structure upon cool-down was argued to be the key to this natural separation mechanism. Additionally, a first-order analysis of the residual thermal stress in the GaN epilayer and sapphire substrate as a function of the GaN deposition thickness was discussed. Such analysis has shown that the post-growth tensile stress in the sapphire substrate increases by about two orders of magnitude for films 1 mm thick, causing the substrate to develop cracks. On the other hand, the compressive thermal stress in the GaN epilayer is reduced by over two orders of magnitude, thus preventing the propagation of cracks generated at the GaN/sapphire interface.

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