GaN Stress Evolution During Metal-Organic Chemical Vapor Deposition

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The evolution of stress in gallium nitride films on sapphire has been measured in real-time during metal organic chemical vapor deposition. In spite of the 16% compressive lattice mismatch of GaN to sapphire, we find that GaN consistently grows in tension at 1050°C. Furthermore, in-situ stress monitoring indicates that there is no measurable relaxation of the tensile growth stress during annealing or thermal cycling.

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The ability to make functional GaN devices on sapphire substrates is remarkable considering the 16% lattice mismatch between GaN and sapphire. Stress in GaN is further compounded by the thermal expansion mismatch between GaN and sapphire. Since stress affects device reliability and bandgap characteristics, and may lead to dislocation generation or even cracking of the film during deposition, the stress evolution of the nitride film is important to understand.

Macroscopic stresses can arise in thin films that are laterally-constrained by a substrate. These stresses are typically classified as being extrinsic, e.g., thermal mismatch stress caused by a difference in the thermal expansion coefficient between the film and substrate, or intrinsic, also referred to as the growth stress [1]. Growth stress results from changes in film density due to microstructure evolution during deposition. Typical causes of growth stresses include heteroepitaxy, island coalescence, grain growth, and surface stress.

A few ex situ, post-growth studies of GaN stress have been performed using X-ray diffraction (XRD) [2,3], wafer curvature [4,5], Raman [4,5], photoluminescence [6], and high resolution transmission electron microscope [7]. All of these studies concluded that the final stress measured at room temperature is less than the predicted compressive thermal stress. A few groups [3,5,6] speculated that GaN is under tension at the growth temperature. Alternatively, it has been suggested that during cool down from the growth temperature GaN partially relaxes its compressive thermal stress [2,4,7]. No direct measurements of the stress during growth have been reported to date.

In this Letter we report direct measurements of the stress evolution in real time during metal organic chemical vapor deposition (MOCVD) of GaN using a wafer
curvature-based technique. We unambiguously show that GaN grows in tension, independent of the buffer material. We also find that annealing and thermal cycling result in no measurable evolution of the growth stress (and implicitly the microstructure). Finally, a comparison of the in situ stress measurements to ex situ room temperature XRD provided a direct measure of the thermal stress.

A high-speed (1200 rpm), inductively heated, Rotating Disk Reactor (RDR) was used to deposit GaN films (nominally 1-3 μm thick) onto 2” diameter, 330μm thick, (0001) sapphire wafers. Trimethylgallium, trimethylaluminum, and ammonia where used as the precursors, with hydrogen as the carrier gas. A detailed description can be found in ref. [8]. A two-step deposition process was used. Initially, a low temperature (LT) buffer of GaN (~550°C) or AlN (~480°C) was grown. The buffer was then heated to 1050°C and stabilized for 1 minute prior to deposition of the high temperature (HT) layer.

Real time wafer curvature measurements were performed with a multi-beam optical stress sensor (MOSS) [9] modified for use on our reactor (Figure 1). To determine the wafer curvature, the divergence of an array of initially parallel laser beams is measured on a CCD camera after reflection of the array from the film/substrate surface. Changes in wafer curvature induce a proportional change in the array spacing on the camera. This technique provides a direct measurement of the stress during deposition and is described in detail in ref. [10].

The relation between film stress ($\sigma_f$), and substrate curvature ($\kappa$), is given by Stoney’s equation [11],

$$\sigma_f h_f = \frac{M_s h_s^2}{6} \kappa,$$

(eq. 1)
where $h_f$ and $h_s$ are the film and substrate thickness, respectively and $M_s$ is the substrate biaxial modulus (Table 1). Curvature is directly proportional to the product of the film stress and film thickness (the "stress-thickness"), both of which vary, in general, during growth. Equation 1 can be derived by balancing the forces and bending moments in the film with those in the substrate, and assuming the film is much thinner then the substrate [1]. We also simultaneously obtain information on the surface roughness and film thickness during deposition by monitoring the intensity of one of the reflected laser beams, similar to the method described in ref. [8].

*Ex situ* XRD was performed to determine lattice constants $c$ and $a$ at room temperature using a $2\theta/\omega$-scans of the (0002) and (20-24) diffraction peaks as outlined in ref. [12]. The strain-to-stress conversion was performed using the expression $\sigma_{xx} = M_s \epsilon_{xx}$, where $M_s$ is the biaxial modulus of the substrate (Table 1). To determine the free standing lattice constants of GaN, a series of undoped elastically strained GaN samples were grown. Free standing lattice constants of $c=5.1850\text{Å}$ and $a=3.1892\text{Å}$ were determined from those samples, in close agreement with the values reported by others [13].

Figure 2 shows the stress-thickness vs. thickness for HT GaN grown on a GaN LT buffer. The slope of the curve defines the incremental stress. We find that GaN grows under a constant tensile stress throughout the entire deposition. The magnitude of the tensile stress ranges from 0.14 GPa to 0.29 GPa from run to run, but is constant during a single deposition. Shown in the same figure is the reflected intensity of the laser spots during growth. The initial dip in the reflected intensity envelope is due to the nucleation and subsequent coalescence ($h_f \leq 0.5\mu m$) of GaN islands [8].
There are several possible origins of the ubiquitous steady-state tensile stress. The simplest explanation is that the HT GaN is pseudomorphic to the thermally strained LT buffer. That is, if the as-grown LT buffer is mostly relaxed and is then heated from 550 °C to 1050 °C, the buffer is placed in a state of tension with a magnitude ≤ 0.6 GPa for GaN on sapphire, onto which the HT GaN film grows coherently. To test this hypothesis, we also deposited HT GaN onto a LT AlN buffer. In this case, where compressive stress (which may be partly or fully relaxed) is expected for GaN on AlN, a key result is that we still measure a tensile stress of the same magnitude as observed for HT GaN on a GaN LT buffer (see inset in Figure 2). Thus, the steady-state tensile stress for GaN on an AlN buffer is inconsistent with the simple explanation of a thermally stressed buffer, since net compression is expected in this case.

In studies of metal films on glass substrates [14], a tensile stress has been attributed to the onset of island coalescence. However, we find that the tensile stress is generated at the earliest stages of HT GaN growth, and remains constant as the film becomes fully continuous. Therefore, the tensile stress observed here cannot be solely attributed to island coalescence. Tensile stresses in some polycrystalline metals have been associated with grain growth [1]. As such, a change in stress occurs during annealing. However, annealing of our GaN films produced no measurable change in stress, suggesting that grain growth is not the main source of the tensile stress.

Further investigation is required to determine the source of the observed tensile stress. We note that increases in tensile stress have been correlated with reductions in defect density obtained using a multiple LT-GaN interlayer structure [15].
Another question debated in the literature is if plastic deformation, driven by the thermal expansion mismatch, occurs in GaN films [2-7]. In order to assess the degree of plastic deformation during cool down [2,4,7], we performed thermal cycling between 1050°C and 450°C on a series of GaN films. When the sample temperature restabilized at 1050°C, the stress returned to the same value as was measured at the end of deposition (Figure 3). This implies that relaxation of the growth stress does not take place during the cool down. We have also annealed GaN immediately after deposition at the 1050°C deposition temperature for 30 minutes and found no significant relaxation of the tensile stress (Figure 3 inset). The small reduction in the stress-thickness product at the end of the anneal quantitatively correlates with a decrease in the reflected intensity that is attributable to a reduction in film thickness. The curvature decrease is therefore associated with hydrogen-assisted film dissociation, not stress relaxation.

The in-situ stress data obtained by MOSS measurements were correlated with ex-situ XRD data. Figure 4 shows the stresses measured at growth temperature (solid squares) by MOSS, at room temperature (solid circles) by XRD, and the difference (solid triangles) from a set of GaN samples with varying stress conditions. The tracking between data at growth and room temperatures clearly establishes MOSS as a viable tool for probing growth stress under MOCVD environment. The absolute difference between the MOSS and XRD results provides the first direct measure of the thermal stress, a value of -0.66 ± 0.1 GPa, associated with cool down from growth to room temperature (provided no relaxation occurs, which was confirmed in the thermal cycling data shown in Figure 3). For comparison, the thermal stress calculated (Table 1) was found to be -1.4 ± 0.7 GPa. We attribute the discrepancy between the measured and calculated results to
inconsistencies in the literature value for the thermal expansion coefficient. The precise tracking between MOSS and XRD (Figure 4) over a range of stresses strongly implies that systematic error in our measurements does not account for this discrepancy.

In conclusion, the evolution of the growth stress in GaN films during deposition has been directly measured via in situ wafer curvature measurement and verified with ex situ XRD. There is a strong tendency for thick HT GaN films on LT GaN and AlN buffers to grow in tension. The tensile stress does not arise from thermal strain imposed by heating the LT buffer to the growth temperature. We find that the growth stress is not relaxed by annealing or thermal cycling.

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(8) J. Han, T. Ng, R. Biefeld, M. Crawford, D. Follstaedt, Appl. Phy. Lett. 71(#21),3114 (1997)
(16) A. Wright, J. Appl. Phys. 82(6), 2833 (1997)
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Figure 1 - Schematic of MOSS system installed on RDR.

Figure 2 - Stress*thickness and reflected intensity vs. thickness for HT GaN on a LT GaN buffer. Shown inset are the stress*thickness and reflected intensity vs. thickness for HT GaN on LT AlN buffer.

Figure 3 - Stress*thickness vs. time during growth and subsequent thermal cycling of a 2.2μm GaN film from 1050°C to 450°C to 1050°C. The stress*thickness and reflected intensity for annealing of a 2.2μm GaN film for 30 min. at 1050°C is shown inset.

Figure 4 - Comparison of stress measured by MOSS during deposition with stress measured by room temperature XRD.

Table 1 - Lattice constants and biaxial modulus for GaN and sapphire

[a] ± 0.0001Å
[b] ± 0.06Å
[c] This is the room temperature value, since HT data on the biaxial modulus was not available.
<table>
<thead>
<tr>
<th>Material</th>
<th>a(T=25°C) Å</th>
<th>a(T=550°C) Å</th>
<th>a(T=1050°C) Å</th>
<th>M<a href="GPa">0001</a></th>
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