

Epitaxial Growth and Orientation of GaN on (1 0 0) γ -LiAlO₂

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Abstract

The (1 0 0) face of γ -LiAlO₂ has attracted attention as a possible substrate for GaN epitaxial growth.

This is partly because this face has an excellent lattice and structural match to (1 $\bar{1}$ 0 0) GaN. This orientation would have a misfit of only -1.4% along the **c**-direction and -0.1% along the **b**-direction of LiAlO₂. We find that in practice this orientation relationship does not occur; instead, (0 0 0 1) oriented GaN grows with a small tilt (0.6° towards the **c**-direction) between the film and substrate. Although the misfit along the substrate **b** direction is large (-6.3%) for this orientation, the tilt perfectly accommodates the -1.4% misfit in the **c** direction. We present characterization of these films by RHEED, X-ray diffraction, and TEM. We propose that the tilt is driven by a reduction of interface energy which occurs in polar, incoherent interfaces.

1. Introduction

The lack of a lattice-matched substrate for epitaxial growth of GaN films has stimulated an intense search for suitable materials. The most commonly used substrate, sapphire, has a very large misfit for GaN, -13.7%. Several alternatives to sapphire have been explored, including SiC [1], spinel [2], ZnO [3] [4], β -LiGaO₂ [5] [6], and γ -LiAlO₂ [7]. β -LiGaO₂ was an obviously promising possibility for GaN epitaxy, because its crystal structure is just a wurtzite superstructure and could be grown by the Czochralski technique. [8] However, β -LiGaO₂ may not be sufficiently stable, particularly at the high temperatures used for MOCVD growth, to be advantageous for GaN growth, and the results that have been obtained with it have been mixed. [9]

γ -LiAlO₂ [a] is chemically similar to β -LiGaO₂. Although the structure [10] is not as closely related to wurtzite, its higher melting point (1700°C [11] vs. 1595°C for β -LiGaO₂ [12]) and the possibility of Czochralski growth [7] have led some crystal growers to pursue its commercial development. Figure 1 shows the crystal structure of tetragonal γ -LiAlO₂. The structure is chiral. The structure can be thought of as a layering of wurtzite {1 $\bar{1}$ 0 0} slabs along the γ -LiAlO₂ **a** azimuth, with Li and Al replacing the Ga in the GaN structure. Alternate slabs are mirror twins. The orientation relationship with GaN [1 $\bar{1}$ 0 0] normal to the γ -LiAlO₂ (1 0 0) surface should thus be favorable. The lattice match to GaN for this orientation relationship is also very good. Along the **c**-direction ([0 0 1]LiAlO₂ || [1 1 -2 0]GaN) the misfit is only -1.4%; along the **b**-direction of γ -LiAlO₂. ([0 1 0]LiAlO₂ || [0 0 0 1]GaN) the misfit would be a minuscule -0.1%. The corresponding misfits for AlN are +1.0%(along **c**) and +3.9% (along **b**).

In this paper we examine the orientation relationships and microstructure for GaN and AlN films grown directly on γ -LiAlO₂. We find that the expected orientation relationship does not occur; instead, **c**-oriented GaN grows with a small tilt towards the γ -LiAlO₂ **c**-axis. We suggest that this tilt is driven by interface energies rather than strain.

2. Epitaxial Growth

The films described here were grown by plasma-assisted molecular beam epitaxy on quarters of a 2 inch (1 0 0) γ -LiAlO₂ substrate provided by Crystal Photonics, Inc. [b] The substrates were cleaned in acetone and methanol, then soldered onto molybdenum heater blocks with indium. The substrates were outgassed at 750°C in vacuum before growth. A normal amount of oxygen outgassing was observed during this stage, and no Li was observed by quadrupole mass spectroscopy. Moderately sharp (1 x 1) reflection high energy electron diffraction (RHEED) patterns, such as shown in Figure 2, were observed from the substrates. It was noted that exposure to the 7.5 keV electron beam resulted in a darkening of a γ -LiAlO₂ substrate. This radiation induced coloring is common in materials with very light elements such as lithium.

GaN was grown using Ga rich conditions similar to those we have previously reported. [13] An RF-coupled nitrogen plasma was used to obtain active nitrogen for MBE growth. A minimal nitridation period of about 10 seconds was used before starting GaN growth. During the time when these films were grown, cross-contamination of our Ga and Mg effusion cells resulted in moderately high Mg doping levels. Silicon contamination from the quartz tube of the plasma source was also present. The substrate temperature for GaN growth was 600°C, and the typical growth rates and film thicknesses were 0.2 μ m/hr and 0.5 μ m, respectively.

We also grew AlN films and GaN films with AlN buffer layers on γ -LiAlO₂. The quality of these films was not as good as the GaN films grown directly on LiAlO₂, as judged by sharpness of RHEED patterns. When grown as a buffer layer, the AlN was grown at a rate of about 0.02 μ m/hr at a nominal substrate temperature of 550°C; when grown as a thick layer, the growth rate was 0.24 μ m/hr at 650°C.

GaN growth was initiated using a Ga flux set to obtain a growth rate of 0.13 μ m/hr on sapphire substrates. The substrate RHEED pattern persisted during the initial stages of growth, gradually fading away as the film RHEED pattern grew brighter. Figure 3(a) shows the pattern after 1 minute of GaN growth directly on a γ -LiAlO₂ substrate. GaN and LiAlO₂ RHEED patterns are superimposed. A faint spot corresponds to a small amount of a second orientation of GaN. After 10 minutes, the gallium flux was increased by a factor of two. At the end of the growth, the GaN displayed a sharp, streaky RHEED pattern. On cooling to about 300°C, a strong «3x3» reconstruction [13] was observed. (Figure 3(b))

3. Film Characterization

3.1. Transmission Electron Microscopy

The microstructure of the film was studied by transmission electron microscopy (TEM) using a Topcon 002B electron microscope with point-to-point resolution of 0.18 nm. The cross-section samples were prepared along [1 0 0] and [1 1 $\bar{2}$ 0] directions. Electron transparency of these samples was obtained by mechanical dimpling followed by argon ion milling at liquid nitrogen temperature. Two-beam conditions allowing defect identification and full-zone conditions for high resolution imaging were applied. Figure 4 shows a cross-sectional image (a) and the corresponding diffraction pattern for the GaN film grown directly on LiAlO₂. The interface is nicely abrupt. The grain size is about 500 nm. Above the interface, a dense network of dislocations is interacting within 150 nm, resulting in dislocation free areas as large as 300 nm near the surface. The main defects are inversion domains and stacking faults. A pseudoperiodic stress contrast is observed in the near-interface region of the substrate. The sample surface is corrugated. In between the GaN grains, there are rather large voids, with faceted pits occurring at grain boundaries.

The diffraction pattern indicates the orientation relationship GaN(0 0 0 1)||LiAlO₂(1 0 0), GaN[1 1 $\bar{2}$ 0]|| LiAlO₂ [0 0 1], GaN[1 $\bar{1}$ 0 0]|| LiAlO₂ [0 1 0]. However a careful examination of the two diffraction patterns reveals a small tilt of the GaN lattice towards the γ -LiAlO₂ <0 0 1>. There is no indication of second phases.

The presence of inversion domains was verified by convergent beam electron diffraction. The predominant GaN orientation was <0 0 0 $\bar{1}$ >, or Ga-face. (The direction from Ga to N in the vertical bonds is away from the substrate.)

3.2. X-ray diffraction

X-ray diffraction was used to determine the precise orientation of the films with respect to the substrate. The measurements were made using a 4-circle diffractometer with monochromatized Cu K α radiation. For the GaN film, only peaks observed in the θ -2 θ scans shown in figure 5 on the substrate normal were the overlapping GaN (0 0 0 2L) and LiAlO₂(L 0 0) peaks. The LiAlO₂(2L+1 0 0) peaks are forbidden by symmetry, but are present, even if they are very weak. These peaks are also observed on bare γ -LiAlO₂ substrates. Measurements of the diffraction from inclined planes confirmed the orientation relationship observed by TEM. An azimuthal scan on the GaN(1 $\bar{1}$ 0 2) planes showed azimuthal full width at half maximums of 0.8-0.9°, compared to an instrumentally limited azimuthal width of 0.25° of the substrate (1 0 1) peaks. No splitting of the GaN(1 $\bar{1}$ 0 2) peak was observed. The centers of the GaN(1 $\bar{1}$ 0 2) peaks are azimuthally aligned to within 0.1° of 60° rotations from LiAlO₂ (0 0 1). There is no measurable diffracted intensity at the 30° positions.

The (rocking curve) scans on unresolved GaN (0 0 0 2) and γ -LiAlO₂(2 0 0) peaks for two perpendicular directions are shown in figure 6. Two peaks are clearly resolved, a sharp peak from the substrate (2 0 0) planes (FWHM=0.16°, instrument limited), and a broader peak (FWHM=0.75°) from the GaN (0 0 0 2) peak. θ -2 θ scans for the tilted peak revealed a 0.15° shift in 2- θ compared to the peak near the substrate normal. A difference of only 0.05° is expected from the difference between the γ -LiAlO₂ (2 0 0) and GaN (0 0 0 2) lattice spacing. These observations confirm the finding from TEM that the film is tilted with respect to the substrate, and give the magnitude of the tilt as 0.56°. Note that the film peak is tilted in only one direction in the substrate **a-c** plane. To check for possible causes of this broken symmetry, we measured the inclination of the surface normal with respect to the crystallographic **a**-axis. This was done by observing the precession around the substrate **a**-axis of a He-Ne laser beam reflected from the surface of the sample during azimuthal rotation. We found that the surface was inclined only slightly, 0.16°, roughly in the substrate **a-c** plane.

Similar measurements were done to check whether the crystallographic tilt was also present in films initiated with AlN. For a GaN film grown on an AlN buffer layer, the tilt was roughly 0.3°. The rocking curve was considerably broader than that of the GaN film grown directly on LiAlO₂, 1.26° compared to 0.75°. For a thick AlN layer grown on an LiAlO₂, the tilt was roughly 0.7°, with a rocking curve FWHM of 2.3°.

3.3. SIMS

A GaN sample grown on a LiAlO₂ substrate was analyzed for Ga and O using secondary ion mass spectroscopy (SIMS) by C. Evans & Assoc. [c] The film was swabbed with methanol to remove any Ga droplets prior to analysis. O was present at a level of approximately 4x10²⁰ cm⁻³ in the film. This level of oxygen impurities is a factor of 10 higher than typical for GaN films grown during the same period of time. However, we cannot exclude the possibility that this high impurity background is unrelated to the substrate material.

3.4. Electrical

The Hall effect was measured to determine the carrier concentration and mobility in the film. The van der Pauw geometry was used. The room temperature mobility was 16 cm²/Vs, with a carrier concentration of 5x10¹⁹ cm⁻³. This low mobility indicates a fairly high level of compensation or disorder.

4. Discussion

The orientation relationship that we observe for GaN on LiAlO₂, GaN(0 0 0 1)||LiAlO₂(1 0 0), GaN[1 1 -2 0]|| LiAlO₂ [0 0 1], GaN[1 $\bar{1}$ 0 0]|| LiAlO₂ [0 1 0], is not surprising in retrospect. Figure 7 shows that the surface meshes for these two orientations are very similar. The misfit for GaN along LiAlO₂ [0 1 0] is -6.3% and along [0 0 1] it is -1.4%. For AlN, the corresponding numbers are -4.0% and +1.0%. Although these numbers are not very low, the misfit for both AlN and GaN is much better than on sapphire, where it is -13.7% and -11.6% for GaN and AlN respectively. It remains to be seen whether the lower misfit can be translated into higher quality films, but it is fair to say that the quality of the films we have grown on LiAlO₂ is not yet as good as films we have grown on sapphire.

The observed tilt of the films is somewhat surprising. The usual picture of misfit accommodation in epitaxial growth is that the film grows in a strained state until the film is so thick that the built-up strain energy surpasses the threshold for dislocation formation. Dislocations often enter as pairs, or as loops. The microscopic tilt associated with each dislocation averages out, resulting in no net tilt, although the small tilts contribute to the mosaic spread as observed in x-ray diffraction rocking curves.

Flinn and co-workers [14] have discussed one way that tilt can accommodate lattice mismatch. The “coherent tilt» that they describe, first observed in the spinel/Al₂O₃ system by Carter and Schmalzried [15], perfectly accommodates one dimensional mismatch if

$$d_f/d_s = \cos\theta_t \quad (1)$$

Here d_f is a film lattice spacing, d_s is the substrate lattice spacing and θ_t is the tilt angle. Note that d_f must be smaller than d_s (positive misfit). If the misfit is negative, coherent tilt would require a miscut surface. The coherent tilt angle for the GaN on LiAlO₂ system is 8.8°, much larger than we observe. In addition, the coherent tilt process cannot explain the tilts we observe for AlN grown on LiAlO₂, since the relevant misfit is negative. Another way that a film might be tilted crystallographically with respect to a substrate is by grapho-epitaxy on a miscut substrate. Here the substrate acts as a physical template for epitaxy, but has very weak chemical bonding to the film. The expected tilt is just the miscut angle. Since the tilt we observe is 3 times the miscut, grapho-epitaxy can only partially explain our results. The small miscut may be responsible for the bias of the tilt we observe; although there is a chirality of the crystal along its *c* axis, it should not be apparent on the (1 0 0) surface.

Another mechanism [16] [17] has been observed to cause very small tilts on miscut substrates. When the film has a larger lattice constant than a miscut substrate, the film tilts to match the step heights on the surface. This is inapplicable to the current system because the step height misfit for *c* GaN on *a* LiAlO₂ is extremely small.

The amount of tilt that would be obtained if all of the misfit dislocations were oriented so that their tilt components added coherently can be simply computed. It is just

$$\sin\theta_t = \Lambda_d (\mathbf{b}\cdot\mathbf{n}) \quad (2)$$

\mathbf{b} is the Burgers vector of the dislocation, \mathbf{n} is the unit vector normal to the substrate and Λ_d is the linear density of dislocations. Only the component of the Burgers vector tangent to the substrate surface is effective at relieving misfit, so there is no generic reason for misfit to give rise to tilt. In the case of coherent tilt the Burger's vector is tilted with the film and thus acquires a component tangent to the substrate surface. For the present case, if we choose Burger's vectors distributed between $(1/3 [1 \bar{1} 0 0] + 1/2 [0 0 0 1])$ and $(1/3 [1 0 \bar{1} 0] + 1/2 [0 0 0 1])$, we obtain a tilt of 0.55° towards $[2 \bar{1} \bar{1} 0]$. This is very close to the tilt we observe. The dislocation spacing should be about 13 nm, which is consistent with the length scale of the strain variation we see by TEM in the LiAlO₂ substrate. Figure 8 illustrates why this particular type of dislocation should be favorable in this system. Without tilt (figure 5a), an interface between the fully relaxed materials will be out of phase every half coherence length, where the coherence length $\lambda_c = a (1/\alpha)$. (α is the misfit.) Because both film and substrate are essentially ionic materials, the interface energy in the out-of-phase regions will be quite high. With tilt, (figure 5b) extra lattice planes are inserted periodically. The GaN structure has an ABAB stacking where each lattice plane is shifted laterally by half a unit cell (a glide plane). Thus a tilt of the right magnitude eliminates the out-of-phase interface regions, drastically reducing the interface energy. By analogy with the “coherent tilt» phenomenon, we can refer to this as “incoherent tilt». Note that since incoherent tilt is driven by interface energies, the dislocations should be energetically favorable even during the first monolayer of growth. This picture is consistent with the observation by RHEED that the growth is immediately incoherent.

Although the observed orientation relationship are not surprising in retrospect, it is still rather surprising that despite the extremely favorable lattice match and structure match there is no tendency at all to form *a* oriented GaN films on the *a* plane of LiAlO₂. Although GaN typically grows with an (0 0 0 1) habit, it is still surprising that not even a small fraction of the GaN would grow in this orientation. Figure 7a and figure 7b show that the structural mismatch for the *c* GaN on *a* LiAlO₂ is entirely in the direction normal to the interface. The white circles in figure 7 represent the dangling bonds on these two surfaces. The match is poor. It is possible that at surfaces or in monolayers, these bonds may hybridize to form a more hexagonal BN-like structure. Future work on the surface structure of LiAlO₂ and on the structure of GaN surface monolayers may resolve this mystery.

5. Conclusion

We have observed the orientation relationships of GaN grown on *a*-plane LiAlO₂ substrates. We find that *c*-oriented GaN and AlN grow with a small tilt in the plane of the nearly lattice matched direction. The magnitude of the tilt is consistent with that required to reduce the interface energy by tilting an incoherent interface. This mechanism for misfit accommodation appears not to have been previously recognized.

There are still a number of unresolved issues. In particular, we have essentially ignored the large misfit along the substrate **b** direction and its effect on the tilt. Even so, control of the incoherent tilt phenomenon may be a way to improve the materials quality of epitaxial films in a variety of large misfit systems, and it may prove fruitful to apply this understanding to the growth of GaN and AlN on sapphire.

Acknowledgments

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Footnotes

[a] In this paper, wherever we refer to "LiAlO₂", we mean "γ-LiAlO₂", just as when we say GaN, we refer to wurtzite GaN.

[b] Crystal Photonics, Inc., 3403 Technological Ave. Suite 14, Orlando FL 32817

[c] S. Mitha, C. Huang, Charles Evans & Associates, 301 Chesapeake Drive, Redwood City CA 94063

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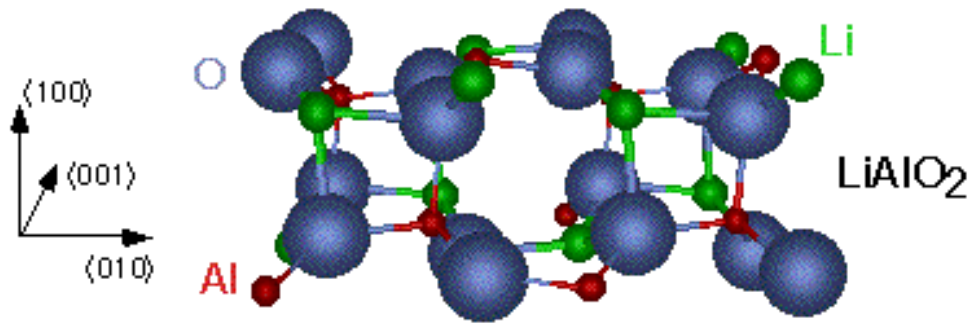


Figure 1a. Crystal structure of γ -LiAlO₂, viewed along the $\langle 001 \rangle$ azimuth.

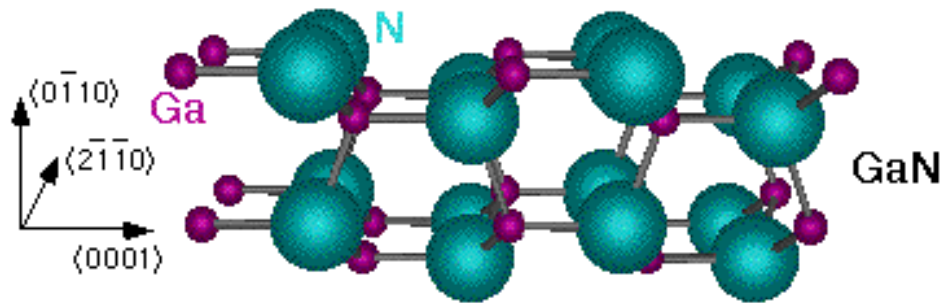


Figure 1b. $(0\ 1\ \bar{1}\ 0)$ surface of GaN. Note the similarity of the layers to the $\{1\ 0\ 0\}$ γ -LiAlO₂ planes.

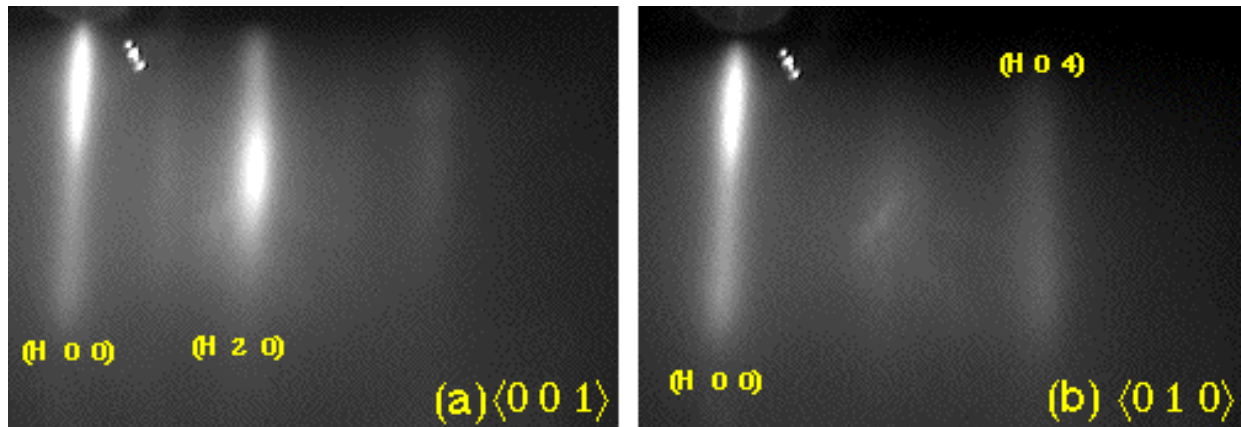


Figure 2. Reflection high energy electron diffraction (RHEED) patterns observed on the γ -LiAlO₂ substrate before growth. (a) $\langle 001 \rangle$ azimuth (b) $\langle 010 \rangle$ azimuth

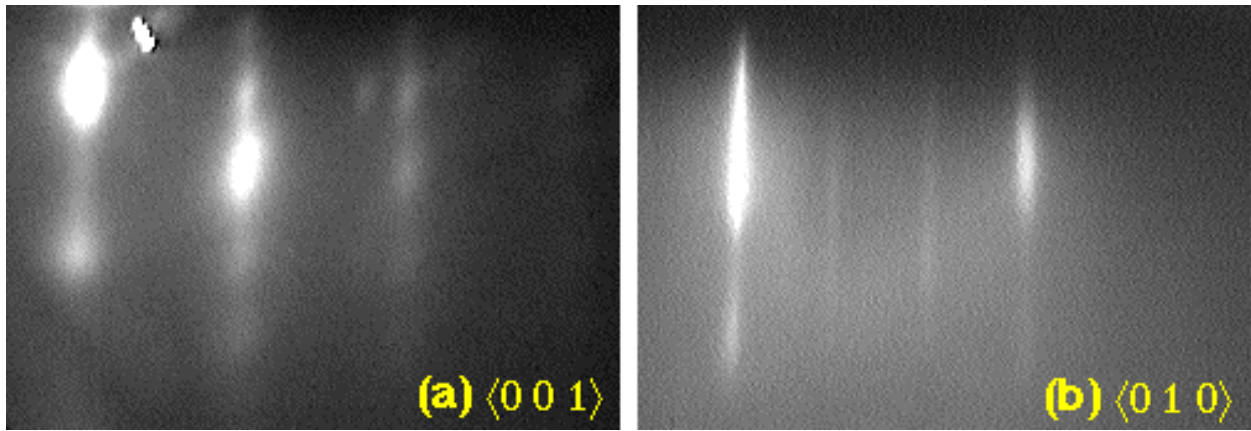


Figure 3. Reflection high energy electron diffraction (RHEED) patterns observed on the γ -LiAlO₂ substrate after GaN growth. (a) after 1 minute GaN growth, viewed on the LiAlO₂ $\langle 0\ 0\ 1 \rangle$ azimuth. The GaN azimuth is $\langle 2\ \bar{1}\ \bar{1}\ 0 \rangle$. GaN and LiAlO₂ RHEED patterns are superimposed. a faint spot corresponds to a small amount of a second orientation of GaN. (b) Cooled to 300°C after growth, along the LiAlO₂ $\langle 0\ 1\ 0 \rangle$ azimuth. The GaN azimuth is $\langle 0\ 1\ \bar{1}\ 0 \rangle$

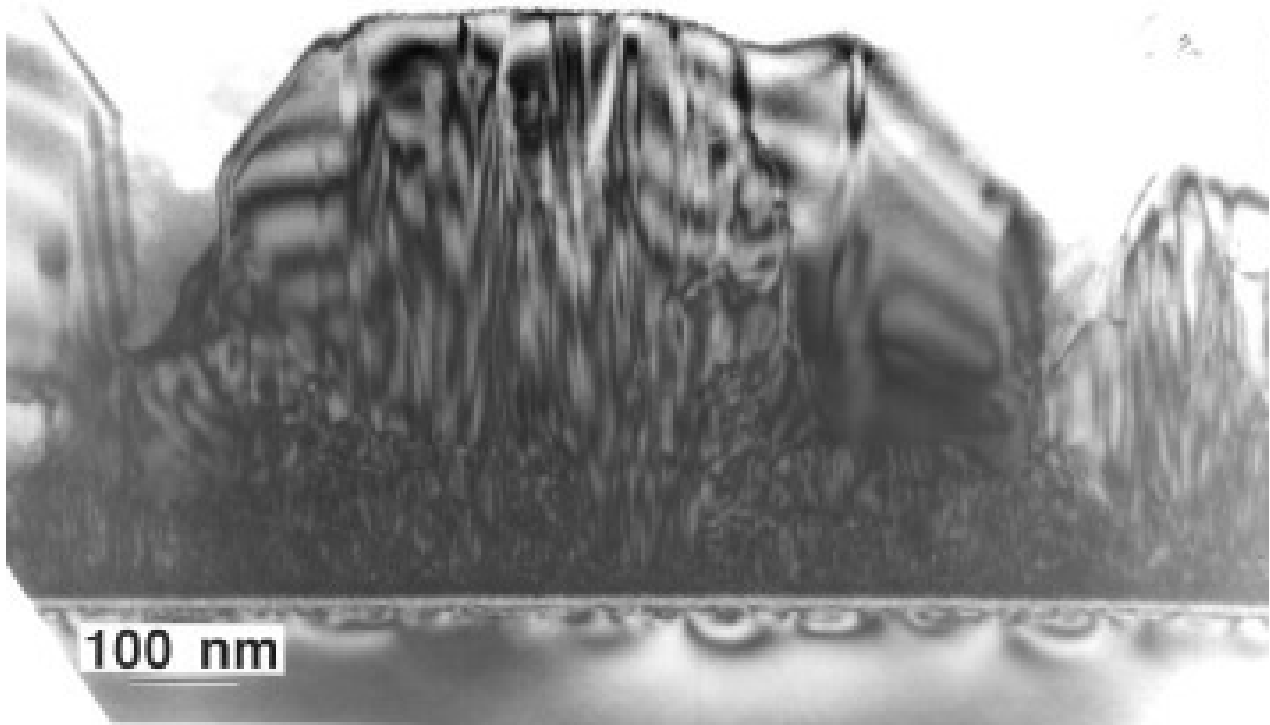


Figure 4a. Transmission electron micrograph of a GaN film grown directly on γ -LiAlO₂. Note corrugated surface of GaN.

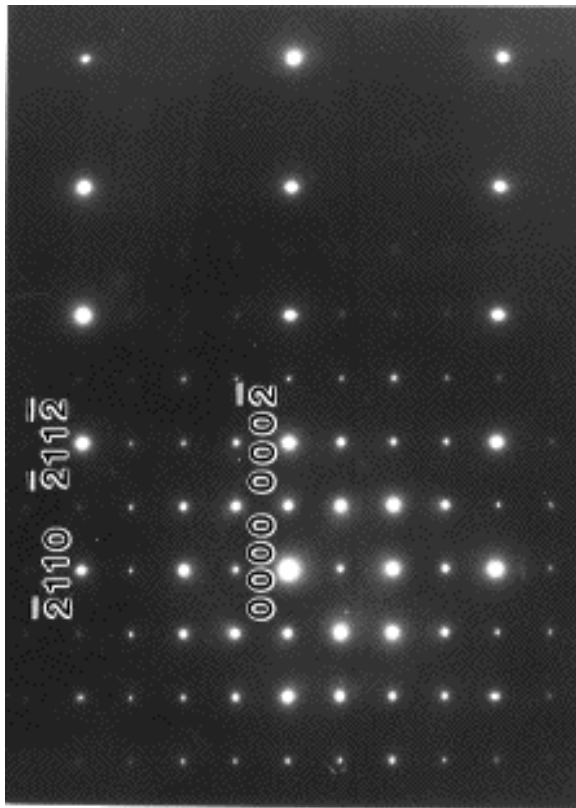


Figure 4b. Diffraction pattern corresponding to the above micrograph. The azimuth is $\text{LiAlO}_2 \langle 0\ 1\ 0 \rangle$. The widely spaced pattern is indexed to the $\text{GaN} \langle 0\ 1\ \bar{1}\ 0 \rangle$ azimuth.

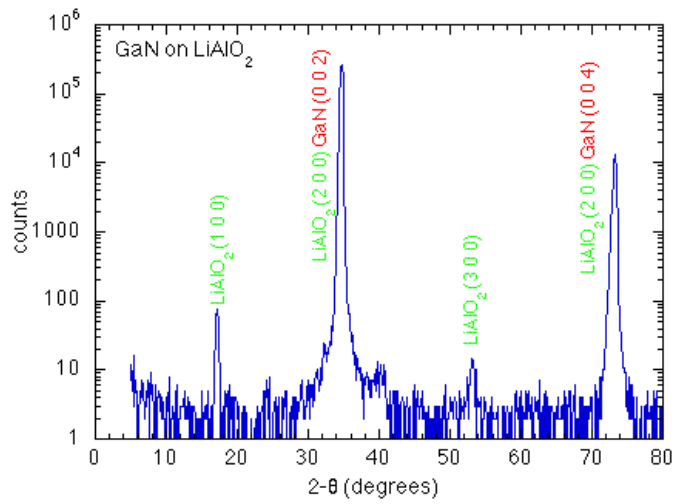


Figure 5. X-ray diffraction θ - 2θ scans from the same $\text{GaN}/\text{LiAlO}_2$ film shown in figure 3 and figure 4.

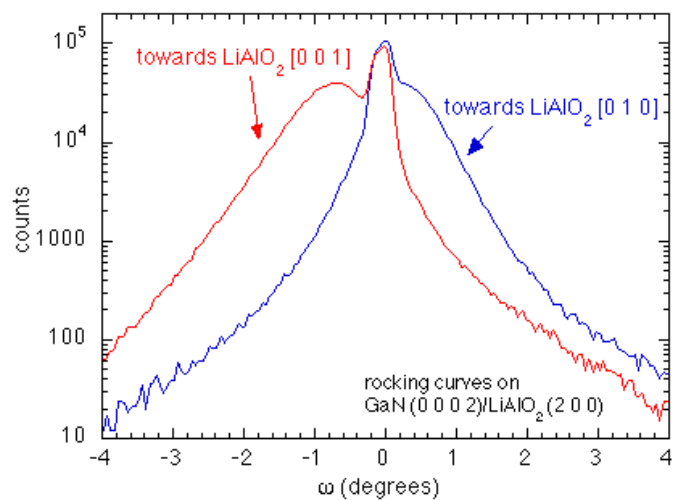


Figure 6. X-ray diffraction rocking curves on GaN (0 0 0 2) and γ -LiAlO₂(2 0 0) peaks for rocking in two perpendicular directions. The LiAlO₂ peak is limited by the instrument resolution.

c

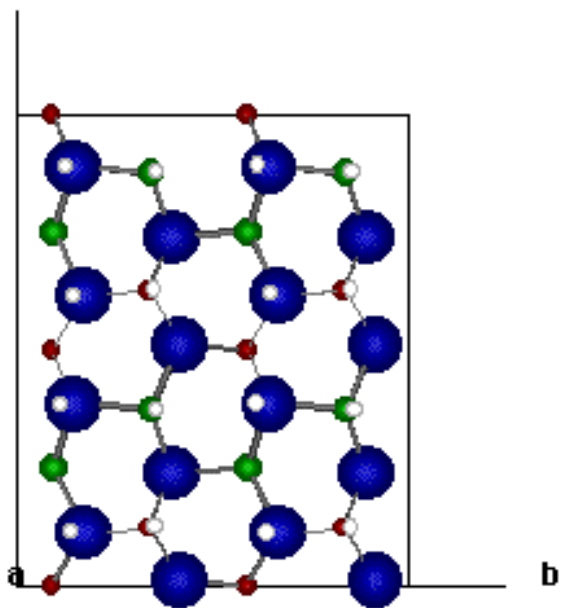


Figure 7a. (1 0 0) surface mesh of γ -LiAlO₂. Note that half the atoms of each type have a dangling bond (denoted by the white circles) pointing out of the surface. Li atoms are green, Al atoms are red, O atoms are blue.

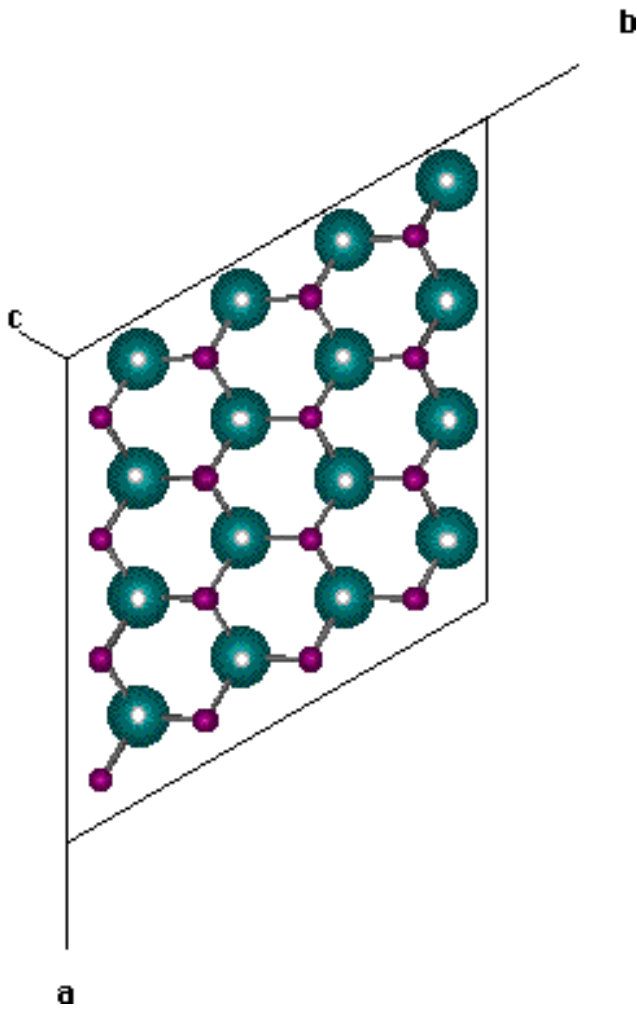
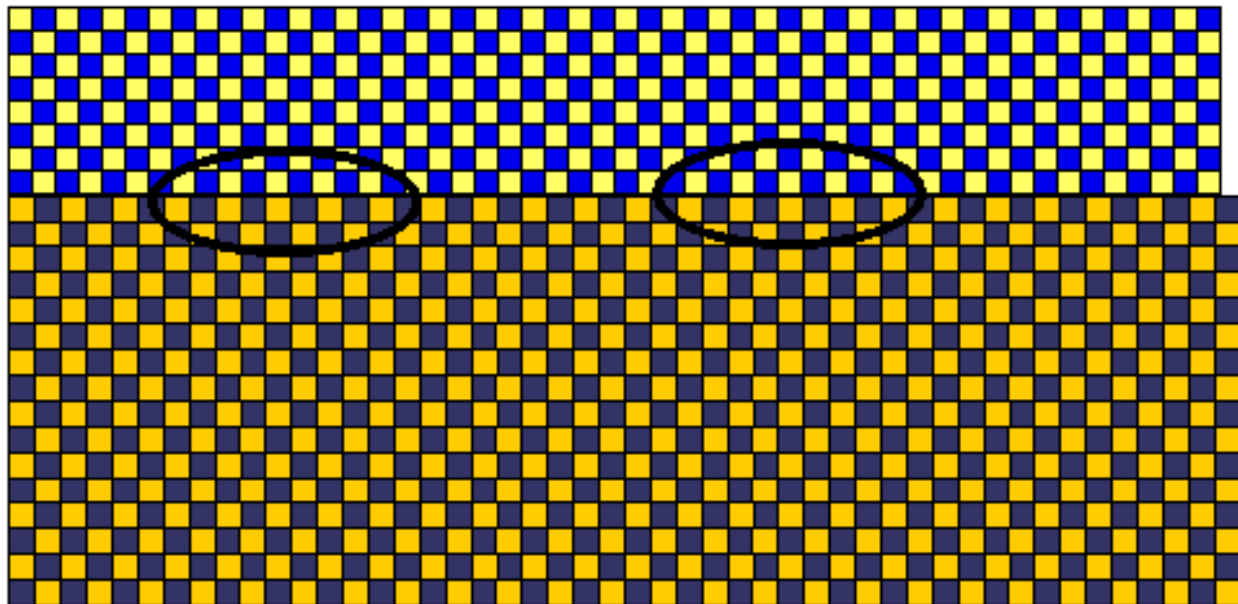
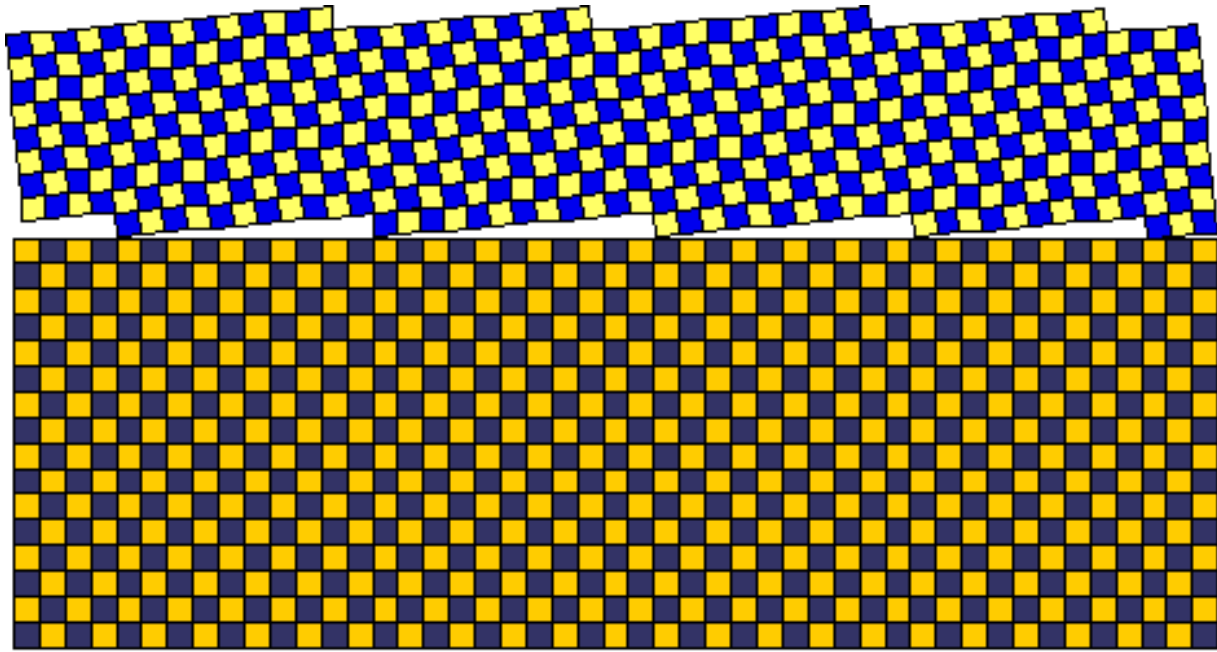


Figure 7b. (0 0 0 1) surface mesh of GaN. Note that either all of the gallium atoms or all of the nitrogen atoms, depending on the polarity, have dangling bonds pointing out. Ga atoms are magenta, N atoms are aqua.



incoherent interface, 10% misfit

Figure 8a. Schematic of a completely incoherent interface with 10% misfit. every half coherence length, the two lattices are exactly out of phase.



incoherent interface with tilt, 10% misfit

Figure 8b. Schematic of an incoherent interface with tilt. Note that the out-of-phase regions are eliminated. This will lower the interface energy in polar crystals.

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